50th ANNUAL MEETING OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLIX MAY 1954 No. 5

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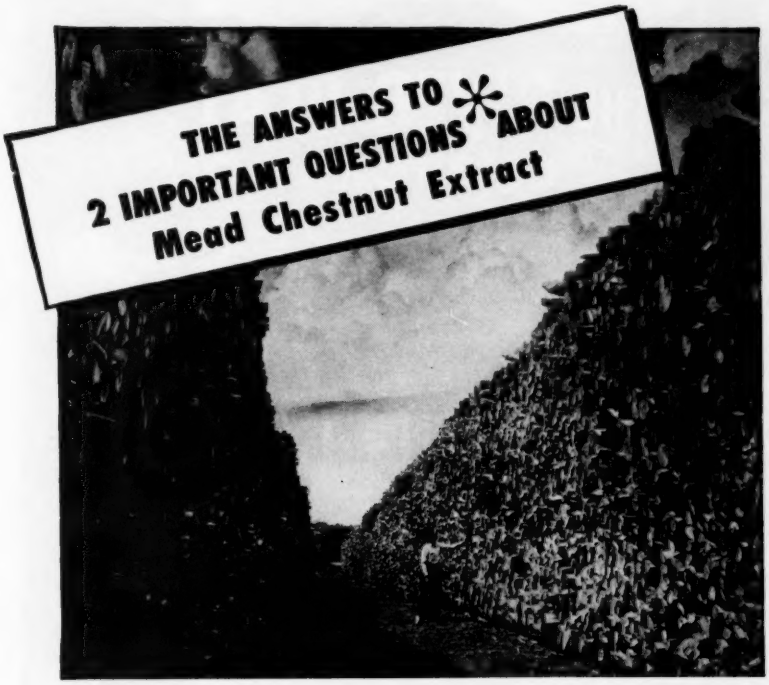

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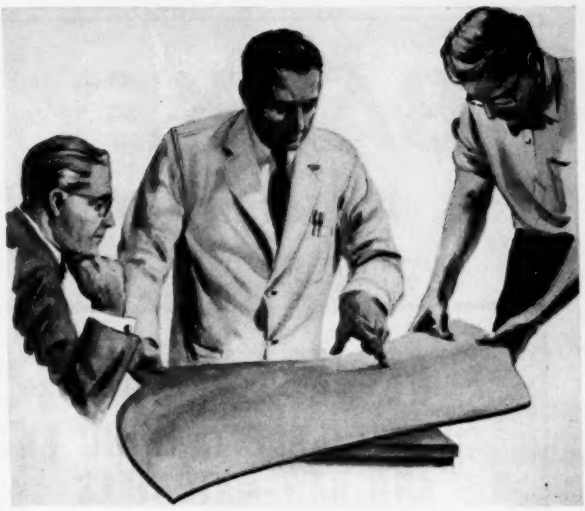

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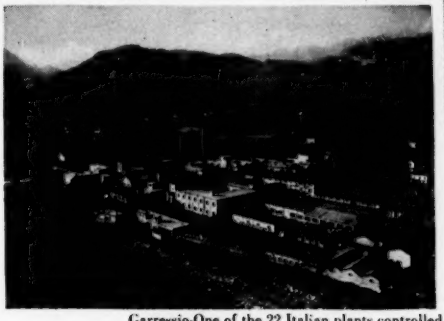

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ALEXANDER SAXE

Alexander Saxe, President of Saxe Cutch Corporation and Saxe Rushworth Company, died in New York on February 11, after a lingering illness. Sandy, as he was familiarly known, had been president of both of the foregoing companies since the death of his father, Sigmond Saxe, in 1944. Sandy was 69 years of age, and was widely known in the leather trade and among A.L.C.A. members. He became an associate member of our organization in 1936, and was a faithful convention attendent.

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Jacques A. Daoust, Duclos-Payan, Ltd., St. Hyacinthe, Que., Canada.
John T. Fitzpatrick, Carbide Research Center, South Charleston 3, West Virginia.
Thomas W. Hathaway, 1844 Brown Avenue, Manchester, New Hampshire.
John M. Jordan, 837 N. Sheridan Road, Waukegan, Illinois.
Irving A. Laub, 1051 Clinton Street, Buffalo, New York.
Saul A. Levine, Colonial Tanning Company, Inc., 730 W. Virginia Street, Milwaukee 4, Wisconsin.
J. D. Lowery, Leather Chemicals Dept., American Cyanamid Company, 30 Rockefeller Plaza, New York 20, New York.
Paul Lutz, Colonial Tanning Company, 730 West Virginia Avenue, Milwaukee 4, Wisconsin.
Martin Stoddard, R. R. No. 1, Grand Haven, Michigan.
Richard F. Payne, Chicago Rawhide Mfg. Company, 1301 N. Elston Avenue, Chicago 22, Illinois.
Michael Phillips, Caroline-Becker, Inc., 40 Herrod Avenue, Brockton, Massachusetts.
Samuel Speigel, Brezner Tanning Corporation, Division of Allied Kid Corporation, Penacook, New Hampshire.
Richard J. Troughton, Whitehall Leather Company, Whitehall, Michigan.
Winton Wm. Willhide, 3037 Magee Avenue, Philadelphia 49, Pennsylvania.
F. A. Wolff, Polychemicals Dept., E. I. du Pont de Nemours & Company, Wilmington, Delaware.

COUNCIL MEETING MINUTES
THE AMERICAN LEATHER CHEMISTS ASSOCIATION

FEBRUARY 11, 1954

HOTEL SYLVANIA
PHILADELPHIA, PENNSYLVANIA

The meeting was called to order by President Turley at 10:00 A. M. All council members were present, also Messrs. Flinn, Teas, Williams, Meo and O'Flaherty.

The minutes of the meeting held on November 10, 1953, were given final approval.

Dr. Turley announced that the Nominating Committee had selected a slate of candidates as prescribed by the by-laws. These have been published in the January, 1954 Journal.

The Awards Committee consisting of Messrs. Maeser, Lord, and Ivany have made selection of the Alsop Award recipient.

As this concludes the work of these two committees, it was requested that the Secretary advise the chairman, with full appreciation of Council for work well done, that their committees have been discharged.

After a discussion of the matter, it was moved, seconded, and carried, that an official delegate be sent to the Meeting of the International Union of Leather Chemists Societies in 1955.

It was then moved, seconded, and unanimously carried, that the sum of $1,000.00 be set aside from the operation surplus of 1953. This $1,000.00 will be invested in government bonds and held for the purpose of defraying the expenses of an official delegate to the Meeting of the International Union of Leather Chemists Societies in 1955. In the event that no delegate is approved by Council, this money will revert to the surplus fund of the Association.

Dr. Flinn stated that a report on the status of technical committees had been published and that these reports covered the present status of the committees.

The following changes were made in the committee membership.

On the Mineral Tanned Leathers Committee, Mr. Robert Adams will become the new chairman, Mr. T. Weaver will succeed Mr. R. Ewe, Dr. R. Stubbings will succeed the late Dr. E. R. Theis, Mr. R. Williams will succeed Dr. R. G. Henrich, Mr. J. Wendkos will succeed Dr. H. G. Turley, and Dr. L. Seligsberger will continue to be a member.

On the Leather Finishes Committee, Mr. Bernard Roll will become the new chairman, and Mr. P. McKee will continue as a member.

On the Tannin Analysis Committee, Mr. G. Stanbery will succeed Dr. E. Flinn.

The Leather Industries of America Advisory Committee was discharged as their cooperation was not utilized.

Dr. Flinn reported on the Methods publication and advised that by July, 1954 all Methods will be published.

Dr. Turley advised that he had accepted the invitation of the Textile Chemists Association for our Association to participate in the Perkins Centennial. The American Leather Chemists Association is to present a panel on "The Dyeing of Leather."

The meeting adjourned for luncheon.

At 1:00 P. M. the meeting was resumed. Council reviewed the financial statements of 1953 and decided to set up a reserve in the surplus account of $1,000.00 from the earned surplus in 1953 to be set aside for defraying the expenses of a delegate to the Meeting of the International Union of Leather Chemists Societies.

Mr. Teas then proposed a detailed budget for 1954 as follows, which was approved by Council.

GENERAL ACCOUNT: INCOME

Dues	$ 10,500.00
Interest on U. S. Bonds	1,000.00
By-Laws and Methods	—0—
Annual Meeting	—0—
Directory	850.00
Total	$ 12.350.00

GENERAL ACCOUNT: EXPENSES	
Executive Secretary's Office Expense	$ 4,200.00
Secretary's Office Expense	1,100.00
Annual Meeting	200.00
Committee Work	100.00
Council Meeting	200.00
Auditing	125.00
Printing Methods and By-Laws	2,000.00
Printing Directory	900.00
Reserve for Uncollectible Accounts	500.00
Winheim Award	—0—
Total	$ 9,325.00
Surplus on General Accounts	$ 3,025.00
JOURNAL ACCOUNT: INCOME	
Advertising	$ 12,000.00
Subscriptions	5,100.00
Journals, volumes, reprints	1,500.00
Dues, S.L.T.C., Difference	800.00
Total	$ 19,400.00
JOURNAL ACCOUNT: EXPENSE	
Printing and Publishing	$ 16,000.00
Printing Reprints	2,100.00
Copyright, Insurance, Storage	500.00
Abstracts and Translations	500.00
Editor's Compensation	1,000.00
Editor's Office Expense	900.00
Advertising Discount	120.00
Total	$ 21,120.00
Deficit on Journal Account	$ 1,720.00

Mr. Meo reported on his plans for the annual meeting, and Council approved the recommended budget of $2,700.00 with the registration fee at $6.00 for members and $12.00 for non-members.

The following people are members of the Convention Committee:

Mr. Dominic Meo	Chairman
Mr. Lauren Meyers	Social
Mr. Ralph Nelson	Hotel
Messrs. R. Weldon and H. Y. Miller	Golf
Mrs. R. Henrich	Ladies

Council approved the plan of selling space for exhibits to firms who desire to do so. The income from such sales is to be used to defray expenses of the annual meeting reception that is to be held on Sunday evening, June 6.

The dates of the annual meeting are Sunday, June 6, through Wednesday, June 9, inclusive.

The Editor, Mr. Williams, reported that the Journal was in good order and he had sufficient papers to complete the August issue.

It was approved by Council that Wednesday, June 9, will be devoted to a practical tanning session, which will be run by a combined committee of the three Production Clubs.

The following members were elected to Active membership:

Dr. Edward Berka
Mr. Inocencio G. Gonzalez, Jr.
Mr. James E. Gore
Mr. R. I. Miller

The following members were elected to Active status from Associate:

Mr. Marden I. Lindsay
Mr. Kenneth P. Monroe
Mr. Richard Williams

Mr. Wilson asked that Council consider the support of committee work which might be accomplished by a paid graduate student. After much discussion the matter was tabled.

Dr. Turley asked Council for its reaction to the simplification and possibly expediting of methods adoption in the by-laws. Council discussed this and the matter was tabled.

There being no further business, Council adjourned at 3:30 P. M.

Respectfully submitted,
FRED O'FLAHERTY, *Secretary*

Methods for the Analysis of Fats, Oils and Their Products

SAMPLING OF FATS AND OILS AND THEIR PRODUCTS (J50)

1. SCOPE

1.1 This method is applicable to the sampling of animal, vegetable and marine fats, and crude and refined animal, vegetable, marine and mineral oils, and products compounded from these materials.

1.2 Methods are given only for barrels, drums and smaller packages. For tank cars and tanks, see Official Methods of A.O.C.S.

2. APPARATUS

2.1 Trier for solid fats, a half-round metal tube ½ to 1 inch in diameter. The length shall be approximately 2 to 5 feet, depending on the size of package to be sampled. One end shall be tapered to a point, the taper to be not more than 1 inch long. The other end shall be attached to a D or T-shaped handle. Copper, brass or bronze must not be used in the construction of this tube.

2.2 Oil thief, a glass tube 3/8 to 1/2 inch inside diameter. The length may be convenient for the size of the package to be sampled. One end shall be constricted by a short taper (not more than 1 inch long) to approximately 1/4 inch. The other end shall be constricted sufficiently so that it can be used as a finger valve. (If the material to be sampled is semi-solid, the constriction at the lower end must be enlarged sufficiently to permit the material to flow into the tube.)

3. SIZE AND NUMBER OF SAMPLES

3.1 General procedure shall be to draw a number of portions from the bulk quantity, or a number of portions from all or several packages, composite these, mix thoroughly and distribute representative portions into suitably sized air-tight containers for the laboratory sample. The number of laboratory samples to prepare shall depend on the circumstances. In all cases involving commercial transactions, a minimum of three shall be required. This permits 1 for the buyer, 1 for the seller and 1 in reserve for possible arbitration.

3.2 A gross sample, in the proportion of not less than 20 pounds for each 100 barrels or equivalent quantity, shall be required when drums, tierces, barrels and other packages are sampled.

3.3 When sampling drums, and all other packages, each package is to be sampled, unless, by agreement of parties concerned, the following schedule may be used.

Number of Packages in Shipment	Number of Packages to be Sampled
1 to 10	1 to 3
11 to 25	2 to 4
26 to 50	3 to 6
51 to 75	6 to 8
76 to 100	8 to 10

In no case shall less than 10 per cent of the packages be sampled.

3.4 In the case of tallows, greases and other fats, the minimum size for each laboratory sample shall be three pounds.

4. GENERAL PRINCIPLES

4.1 Directions for sampling fats and oils, that will encompass all conditions and circumstances, are impossible to write. There are many instances in which the experience and judgment of the individual doing the sampling must prevail. However, certain general rules must govern if the sample is to be representative.

4.2 Best samples of oil in bulk or in packages are obtained if the product is completely liquid and thoroughly mixed. Shipments of oil received in cold

weather must be allowed to warm up to the extent that all the contents are liquid before sampling is attempted.

4.3 If the physical structure of the product is involved, such as the consistency of Sponging Compound, the material must not be softened, melted or sampled with any of the devices mentioned in par. 2. In such cases, the cover of the container shall be removed and a section cut out with a spatula or removed with a dipper, with as little disturbance to the surface as possible. However, additional sampling shall be carried out in the regular manner, as described in par. 5., for sample requirements for all other tests or analyses.

4.4 If the stability or keeping quality of the product is involved, all equipment and containers must be scrupulously clean. Containers may be new tinned cans or glass jars depending on the product. No metal, such as copper, bronze and brass, shall be allowed to come in contact with the sample.

4.5 All samples shall be completely labeled for identification.

5. PROCEDURE

5.1 *Barrels, tierces, casks and drums; liquid or semi-liquid contents.* The container shall be rolled to mix the contents and the oil thief slowly inserted through the bung or preferably through an end opening or hole drilled at one end. If possible, the sample should be drawn from end to end.

5.1.1 It is necessary that, as the oil thief is lowered into the oil, the rate be slow enough so that the level of oil inside and outside of the thief remains the same. Otherwise, an unduly large portion will be drawn from the bottom which may contain a concentration of moisture and/or settlings.

5.1.2 As soon as the thief is fully inserted, the upper constriction shall be closed with a finger and the sample shall be transferred into a suitable container. Several portions shall be taken in this manner from this and other packages as directed in par. 3.3. Before distribution into laboratory sample containers, the sample shall be mixed thoroughly.

5.2 *Barrels, tierces, casks and drums or other packages; solid contents.* The bung or end opening shall be removed or a hole shall be drilled through an end or side, with auger, large enough in diameter to accommodate the trier. If possible, the sample shall be drawn from end to end.

5.2.1 The trier shall be inserted through the opening, pushing it through to the opposite end or side, after which it shall be turned in a complete circle and withdrawn with the sample. Several portions shall be collected from this and other packages as directed in par. 3.3. Before distribution into laboratory sample containers, the sample shall be softened (but not melted) and mixed thoroughly.

5.3 *Barrels, tierces, casks, bags or other packages, very hard materials.* If the material is in the form of flakes or small pieces, grab samples shall be taken of uniform and proportional size from packages as directed in par. 3.3.

If the material is in large pieces, these shall be broken up before taking the grab sample. After mixing thoroughly and quartering, the samples shall be distributed into laboratory sample containers.

6. HISTORY

6.1 The method has been adapted from the official methods of the American Oil Chemists Society.

A.L.C.A. Provisional Method, March 1954

FATS, AND OILS OF ANIMAL, VEGETABLE AND MARINE ORIGIN — GENERAL (H1)

1. SCOPE

1.1 This method is intended to identify the analytical procedures normally employed in the analysis of fats and oils of animal, vegetable and marine origin.

1.1.1 The natural fats and oils consist primarily of triglyceryl esters, usually referred to as triglycerides or triglyceride oils, thereby distinguishing them from waxes and petroleum oils and greases. The methods employed are equally applicable to the partial esters of glycerol and the glycols.

1.1.2 It is conventional to refer to fats as those triglycerides which are solid or semi-solid at room temperature and to oils as those which are liquid under the same condition.

1.2 The methods have not been developed with special reference to waxes, such as beeswax, carnauba wax, wool wax, (common degras), but some of the procedures may be found applicable to these substances.

2. SPECIMEN

2.1 The fats and oils shall be sampled in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 The volumetric glassware, reagents and distilled waters employed, shall conform to the specifications outlined in par. 3, Methods A1 and F1.

4. PROCEDURE

4.1 *Moisture.* Moisture shall be determined by the xylene distillation procedure as outlined in Method H40.

4.2 *Moisture and Volatile Matter.* Moisture and volatile matter shall be determined by the hot plate method as in Method H20.

4.3 *Insoluble Impurities.* Insoluble impurities shall be determined as in Method H21.

4.4 *Ash.* Ash shall be determined as in Method H22.

4.5 *Specific Gravity.* Specific gravity shall be determined as in Method H15.

4.6 *Melting Point.* The melting point shall be determined as in Method H16.

4.7 *Titer Test.* The titer test shall be determined as in Method H17.

4.8 *Cloud and Pour Point.* The cloud and pour point shall be determined as in Method H18, except that the thermometer readings shall be taken every 2°F. instead of 5°F.

4.9 *Free Fatty Acids.* The free fatty acids shall be determined as in Method H30.

4.10 *Saponification Value.* The saponification value shall be determined as in Method H31.

4.11 *Iodine Value.* The iodine value shall be determined as in Method H32.

5. HISTORY

5.1 With the exception of the procedures for moisture and for cloud and pour points, the methods employed have been adapted from the official methods of the American Oil Chemists Society for fats and oils of animal, vegetable and marine origin.

5.2 Procedures for moisture (A.S.T.M. Designation: D 500-45) and cloud and pour points (A.S.T.M. Designation: D 97-47) are standard methods and are published by permission of American Society for Testing Materials, 260 S. Broad Street, Philadelphia, Pa.

A.L.C.A. Provisional Method, March 1954

HARD GREASES — GENERAL (H2)

1. SCOPE

1.1 This method is intended to identify the analytical procedures normally employed in the analysis of hard greases.

1.2 Hard greases for purposes of these analyses are defined as mixtures of fats, containing none to considerable quantities of oil, wax or similar materials. Such greases may contain substantial amounts of unsaponifiable matter.

2. SPECIMEN

2.1 The hard greases shall be sampled in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 The volumetric glassware, reagents and distilled waters employed, shall conform to the specifications outlined in par. 3, Methods A1 and F1.

4. PROCEDURE

4.1 *Melting Point.* The melting point shall be determined as in Method H16.

4.2 *Free Fatty Acids.* The free fatty acids shall be determined as in Method H30, with the following changes. The sample size shall be increased by a percentage equal to the estimated proportion of unsaponifiable matter in the grease. Depending on the size of the sample, 25 to 50 ml. of petroleum ether shall be added, in addition to the neutralized alcohol and indicator, to insure better contact of the free fatty acids with the titrating solution. The sample should be completely dissolved in the solvents before beginning the titration, using heat to effect solution if necessary.

4.3 *Saponification Value.* The saponification value shall be determined as in Method H31, with the following changes. The sample size shall be increased by a percentage equal to the estimated proportion of unsaponifiable matter in the grease. Depending on the size of the sample, 75 to 100 ml. of petroleum ether shall be added to the sample, in addition to the neutralized alcohol and indicator, in order to insure better contact of saponifiable matter with the alkali during refluxing. A larger size flask than specified may be required also. A blank determination shall be prepared and run simultaneously with the sample and similar in all respects. Refluxing shall be done for a minimum period of 1.5 hours.

4.4 *Unsaponifiable Matter.* The unsaponifiable matter shall be determined as described in Method H47 or as briefly outlined in par. 4.4.1.

4.4.1 Into a 300 ml. flask shall be accurately weighed 5 grams of sample to which is added 5 ml. of 50 per cent solution of potassium hydroxide, 25 ml. of 95 per cent alcohol and 25 ml. of petroleum ether. The mixture shall be boiled, using a reflux condenser, for a minimum period of 1.5 hours, shaking occasionally and using glass beads to prevent bumping, if necessary. 50 ml. of hot water shall then be added, and after cooling, the whole shall be transferred to a separatory funnel and extracted three times, using 40 ml. of petroleum ether for each extraction. The combined petroleum ether solution shall be washed three times with a mixture of 30 ml. of water and 10 ml. of 95% alcohol for each washing. The petroleum ether shall then be transferred to a tared dish, evaporated to dryness, avoiding excessive drying, cooled and weighed. Results shall be expressed as per cent unsaponifiables.

5. HISTORY

5.1 With the exception of unsaponifiable matter (A.S.T.M. Designation: D 500-45), the methods employed have been adapted from the official methods

of the American Oil Chemists Society for fats and oils of animal, vegetable and marine origin.

A.L.C.A. Provisional Method, March 1954

MOELLON — GENERAL (H3)

1. SCOPE

1.1 This method is intended to identify the analytical procedures normally employed for moellons.

2. SPECIMEN

2.1 The moellons shall be sampled in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 The volumetric glassware, reagents and distilled waters employed, shall conform to the specifications outlined in par. 3, Methods A1 and F1.

4. PROCEDURE

4.1 *Moisture.* Moisture shall be determined as in Method H40.

4.2 *Ash.* The moellon shall be ashed in accordance with Method H22.

4.3 *Sediment.* Sediment shall be determined as in Method H23 which is a modification of A.S.T.M. Designation: D 473-48 and Method 300.2.2 of Federal Specification VV-L-791d.

4.4 *Unsaponifiable Matter.* Unsaponifiables shall be determined as outlined in par. 4.4, Method H2.

4.5 *Free Fatty Acids.* Free fatty acids shall be determined as in Method H30 (modified in accordance with par. 4.2, Method H2).

4.6 *Total Oxidized Fatty Acids.* The soap solution, remaining from the unsaponifiable determination shall be boiled until all the alcohol is expelled. Then dissolve in hot water and transfer to a separatory funnel, rinsing the beaker thoroughly and bringing the volume to about 300 ml. Immediately an excess of concentrated hydrochloric acid shall be added, using about 25 per cent more than sufficient to neutralize the total alkali. After rotating the flask vigorously, cooling, and shaking out with petroleum ether, the aqueous layer shall be run off and the ether layer shall be poured off, avoiding loss of oxidized fatty acids.

4.6.1 The acids shall then be washed twice with a small quantity of petroleum ether and twice with a small quantity of hot water and finally dissolved in warm 95 per cent alcohol. The alcohol solution shall be filtered, if necessary, transferred to a tared dish and dried in an evaporator and dryer

for 16 hours. After cooling and weighing, the results shall be expressed as per cent oxidized fatty acids. The entire determination should be conducted without delay.

A.L.C.A. Provisional Method, March 1954

COMPOUNDED OILS — GENERAL (H4)

1. SCOPE

1.1 This method is intended to identify the analytical procedures commonly used for compounded oils.

1.2 Compounded oils are defined as fatty oils which are liquid at normal room temperature, and which contain mineral oil, wax, or similar added materials.

2. SPECIMEN

2.1 Compounded oil shall be sampled in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 The volumetric glassware, reagents and distilled waters employed shall conform to the specifications outlined in par. 3, Methods A1 and F1.

4. PROCEDURE

4.1 *Free Fatty Acids.* The free fatty acids shall be determined as in Method H30 (modified in accordance with par. 4.2, Method H2.)

4.2 *Saponification Value.* The saponification value shall be determined as in Method H31 (modified in accordance with par. 4.3, Method H2).

4.3 *Unsaponifiable Matter.* Unsaponifiables shall be determined as outlined in par. 4.4, Method H2.

4.4 *Cloud and Pour Point.* Cloud and pour points shall be determined as in Method H18, except that thermometer readings shall be taken every 2°F. instead of 5°F.

A.L.C.A. Provisional Method, March 1954

SULFONATED AND SULFATED OILS — GENERAL (H5)

1. SCOPE

1.1 This method is intended to identify the procedures for the chemical analysis of sulfonated and sulfated oils.

2. SPECIMEN

2.1 The sulfonated and sulfated oils shall be sampled in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 The volumetric glassware, reagents and distilled waters employed, shall conform to the specifications outlined in par. 3, Methods A1 and F1.

4. PROCEDURE

4.1 The various analytical procedures employed are listed in the following table with the reference method number.

Analytical Procedure	Method Number
Moisture (Distillation method)	H40
Moisture and Volatile Matter (Hot plate test)	H41
Organically Combined Sulfuric Anhydride	
1. Titration Tests (for sulfated oils)	H42
2. Extraction-Titration Test, (for sulfated oils)	H43
3. Ash-Gravimetric Test, (in presence of true sulfonates)	H44
Total Desulfated Fatty Matter, (for sulfated oils)	H45
Total Active Ingredients	H46
Unsaponifiable Non Volatile Matter	H47
Inorganic Salts	H48
Total Alkalinity and Total Ammonia	H49
Acidity as Free Fatty Acids or Acid Number	
1. In absence of Ammonium or Triethanolamine Soaps	H50
2. In presence of dark colored oils but in the absence of Ammonium or Triethanolamine Soaps (Brine Test)	H51
3. In presence of Ammonium or Triethanolamine Soaps	H52
Neutral Fatty Matter	H53

5. HISTORY

5.1 These methods are the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45) of the American Society for Testing Materials and are adopted as Methods of the American Leather Chemists Association with the following modifications. Section 60 to 65 "Water-Immiscible Organic Solvents Volatile with Steam" have been omitted. Modifications have been made to the procedure for "Desulfated Fatty Matter" (Method H45) and a method for "Neutral Fatty Matter" has been added (Method H53).

5.2 These methods are published by permission of American Society of Testing Materials, 260 S. Broad Street, Philadelphia, Pa.

A.L.C.A. Provisional Method, March 1954

COMMERCIAL SOAP AND SOAP PRODUCTS (H6)

1. SCOPE

1.1 The methods of the American Oil Chemists Society for Sampling and Analysis of Commercial Soaps and Soap Products have been adopted as Official Methods of the A.L.C.A.

1.2 Copies of these methods can be purchased from American Oil Chemists Society, 705 Tchonpitonlas Street, New Orleans, La.

A.L.C.A. Official Method 1942

SPONGING COMPOUNDS — GENERAL (H7)

1. SCOPE

1.1 This method is intended to identify the analytical procedures commonly employed to appraise a sponging compound.

2. SPECIMEN

2.1 The sponging compounds shall be sampled in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 The volumetric glassware, reagents and distilled waters employed, shall conform to the specifications outlined in par. 3, Methods A1 and F1.

4. PROCEDURE

4.1 *Consistency.* The original compound shall be smooth to the feel and contain no granular particles.

4.2 *Moisture.* Moisture shall be determined as in Method H40.

4.3 *Ash.* The sponging compound shall be ashed in accordance with Method H22.

4.4 *Unsaponifiable Matter.* A 10 gram sample shall be saponified by refluxing for one hour with 50 ml. of 0.5 *N* potash solution made with ethylene glycol mono ethyl ether instead of alcohol [see *Analyst*, 61, 687 (1936) and *J.A.L.C.A.*, 32, 185 (1937)], or with a strong alcoholic potash solution as recommended by Lewkowitsch for carnauba wax. After saponification, the analysis shall proceed as in Method H47.

4.5 *Nitrogen.* Nitrogen shall be determined as in Method B5, except that a 5 gram sample shall be employed. In the calculation of results, *N* x 6.38 = albumin.

4.6 *Total Alkali.* Total alkali shall be determined as in Method H49.

4.7 *pH of* 10 *Per Cent Emulsion.* Ten grams of sample shall be emulsified in 100 ml. of boiling water, cooled and the pH determined electrometrically.

4.8 *Stability of* 10 *Per Cent Emulsion.* A ten gram sample shall be emulsified with sufficient water at 60° to 65°C. to make 100 ml. After standing overnight in a 100 ml. graduated cylinder, observe whether any free oil or grease shows and record the thickness of the layer of "cream".

4.9 *Total Grease.* Total grease shall be calculated as follows

$$\text{Total grease and waxes} = 100 - (A + B + C)$$

where A = volatile matter
B = ash
C = nitrogen as glue or casein

4.9.1 The greatest inaccuracy in this procedure is that the soda probably appears as Na_2CO_3, in the ash, and would, therefore, tend towards lower results for total grease. On the other hand, if NaCl is present, too high an ashing temperature will lead to the volatilization of some of the NaCl. It is believed that the indirect method (stated in par. 4.9) is to be preferred to decomposition with acids, followed by a variety of solvents to assure solution of paraffin, greases, carnauba wax, etc.

A.L.C.A. Provisional Method, March 1954

MINERAL OIL — GENERAL (H8)

1. SCOPE

1.1 This method is intended to identify the analytical procedures normally used to examine mineral oils employed in the leather industry.

2. SPECIMEN

2.1 The samples shall be procured in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 The volumetric glassware, reagents and distilled waters employed shall conform to the specifications identified in par. 3, Methods A1 and F1.

4. PROCEDURE

4.1 *Evaporation Loss.* About 5 g. of sample shall be weighed accurately into an official tannin dish and the whole heated for 16 hours in a combined evaporator and dryer, or other oven used for drying tannin analysis residues (see Method A13, par. 2.). The dish shall then be cooled in a desiccator and weighed. The results shall be calculated as the loss in weight in per cent of the original oil.

4.2 *Cloud and Pour Points.* The cloud point and pour points of mineral oil shall be determined as in Method H18.

A.L.C.A. Provisional Method, March 1954

SPECIFIC GRAVITY OF OILS AND LIQUID FATS (H15)

1. SCOPE

1.1 This method is intended to determine the specific gravity of the sample in liquid form as compared with water at 25°C. and is applicable to all oils and liquid fats.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

3. APPARATUS

3.1 Specific gravity bottles, approximately 50 ml. capacity, with well fitting ground glass joints.

3.1.1 These bottles shall be calibrated as follows: Clean and dry thoroughly and then fill with recently boiled and cooled distilled water at 20° to 23°C. Fill the bottle to overflowing by holding the bottle on its side in such a manner as to prevent the entrapment of air bubbles. Insert the stopper and immerse in water bath at 25°C. ± 0.2°C. Keep the entire bulb completely covered with water and hold at specified temperature for 30 minutes. Carefully remove any water which has exuded from the side opening. Remove the bottle and contents and calculate the weight of water in the flask by subtracting the weight of empty bottle from the weight of bottle plus water.

3.2 Water bath maintained at 25°C. ± 0.2°C.

3.3 Thermometer, of suitable range with 0.1° or 0.2° subdivisions. The thermometer shall be standardized carefully, preferably by comparison with a thermometer calibrated by the U. S. Bureau of Standards.

4. PROCEDURE

4.1 *Specific Gravity at 25/25°C.* The sample shall be melted and filtered through filter paper to remove any impurities and the last traces of moisture. The sample shall be completely dry. After cooling the sample to 20° to 23°C., the bottle shall be filled to overflowing, holding the bottle on its side in such a manner as to prevent the entrapment of air bubbles.

4.1.1. Fats not liquid at 25°C. shall be tested at 60/25°C.

4.2 After inserting the stopper, the bottle shall be immersed and held in the water bath at 25° ± 0.2°C. for 30 minutes. Any oil, which has come

through the capillary opening shall be carefully wiped off and the bottle shall be removed from the bath and cleaned and dried thoroughly.

4.2.1 Unless the specific gravity bottles are protected with caps, care must be taken so that no oil (or calibration water as in par. 3.1.1.) is lost in the interval between removal from the bath and weighing. If the temperature of the room is above 25°C., this may happen, and even the warmth of the hand surrounding the bottle is sufficient to cause expansion of the contents of the flask.

4.3 The bottle and contents shall then be weighed and the specific gravity calculated as directed in par. 5.1.

4.4 *Specific Gravity at* 60/25°C. The procedure is the same as described in par. 4.1 except that the melted fat shall be poured into the specific gravity bottle at 56° to 58°C.

4.5 The bottle, containing the sample, shall be allowed to remain in the bath at 60° ± 2°C. for 30 minutes and then shall be cooled to room temperature and weighed. The specific gravity shall be calculated as in par. 5.2.

5. RESULTS

5.1 The calculation of specific gravity at 25/25°C. shall be made as follows

$$\text{Specific gravity (25/25°C.)} = \frac{A - B}{\text{Weight of water at 25°C.}}$$

where A = weight of bottle and oil
B = weight of bottle

5.2 Specific gravity at 60/25°C. shall be calculated as follows

$$\text{Specific gravity (60/25°C.)} = \frac{A - B}{W\ [1 + (0.000025 \times 35)]}$$

where A = weight of bottle and oil (60°C.)
B = weight of bottle (60°C.)
W = weight of water (25°C.)

5.2.1 Unless the specific gravity bottles are made of glass with a very low coefficient of expansion, a correction shall be made for the expansion of the glass. The coefficient of expansion of ordinary glass is approximately 0.000025.

6. HISTORY

6.1 This method has been adapted from the official methods of the American Oil Chemists Society, for fats and oils of animal, vegetable and marine origin.

A.L.C.A. Provisional Method, March 1954

MELTING POINT (H16)

1. SCOPE

1.1 This method is intended to determine the melting point of all normal animal and vegetable fats.

1.2 The natural fats and oils, that is those of animal and vegetable origin, are mixtures of glycerides and other substances and consist of a number of components. They do not exhibit either a definite or sharp melting point. Fats pass through a stage of gradual softening before they become completely liquid. The melting point then shall be defined by the specific conditions of the method by which it is determined and, in this case, it shall be the temperature at which the sample becomes perfectly clear and liquid.

2. SPECIMEN

2.1 The specimen taken for melting point shall be sampled in accordance with Method J50.

3. APPARATUS

3.1 Melting point tubes, capillary glass tubing, inside diameter 1 mm., outside diameter 2 mm. maximum, convenient length 50 to 80 mm.

3.2 Thermometer (see specification for Titer Thermometer, Method H10).

3.3 Glass beaker, 600 ml.

3.4 Heat source, gas burner or electric hot plate with rheostat control.

4. PROCEDURE

4.1 The sample shall be melted and filtered through filter paper to remove any impurities and the last traces of moisture. The sample shall be absolutely dry. At least three (3) clean capillary tubes shall be dipped in the completely liquid sample so that the fat stands approximately 10 mm. high in each tube. One end of the tube (where the sample is located) shall be fused in a small flame, taking care not to burn the fat.

4.2 The tubes shall be placed in a beaker and held in a refrigerator at 4° to 10°C. (40° to 50° F.) overnight (16 hours).

4.2.1 The samples shall be completely liquid when the tubes are placed in the refrigerator. It is good practice to pass the ends of the tubes containing the sample momentarily through the flame just before they are taken to the refrigerator.

4.3 After removing from the refrigerator, the tubes shall be attached to the thermometer, using a rubber band or any suitable means, so that the lower ends of the melting point tubes shall be even with the bottom of the mercury bulb of the thermometer. The thermometer shall be suspended in a 600 ml. beaker, which is about half full of clear distilled water and the bottom of the thermometer immersed approximately 30 mm.

4.4 The starting bath temperature shall be adjusted to 8° to 10°C. below the melting point of the sample at the beginning of the test. Agitation of the water bath shall be made with a small stream of air or other suitable means, and heat shall be applied so the bath temperature is increased at the rate of approximately 0.5°C. (1°F.) per minute.

4.5 Fats usually pass through an opalescent stage before melting completely. The heating shall be continued until the tubes are completely clear throughout. The temperature shall be observed at which each tube becomes clear.

5. RESULTS

5.1 The average of the melting point of all the tubes shall be taken and this average shall be reported as the melting point.

6. HISTORY

6.1 This method has been adapted from the official methods of the American Oil Chemists Society, for fats and oils of animal, vegetable and marine origin.

A.L.C.A. Provisional Method, March 1954

TITER TEST (H17)

1. SCOPE

1.1 This method is intended to determine the solidification point of the fatty acids and is applicable to normal animal and vegetable fats and oils and marine oils.

2. SPECIMEN

2.1 The sample shall be obtained in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 Griffin low-form beaker, 2-liter capacity.

3.2 Wide mouth bottle, capacity 450 ml., height 190 mm. inside diameter of neck 38 mm.

3.3 Test tubes, length 100 mm., diameter 25 mm., with or without rim. These tubes may have an etched mark extending around the tube at a distance of 57 mm. from the bottom to show the height to which the tube is to be filled.

3.4 Saponification vessel, use a 750 or 1000 ml. flask.

3.5 Stirrer, 2 to 3 mm. outside diameter with one end bent in the form of a loop of 19 mm. outside diameter. Glass, nichrome, stainless steel or monel

wire shall be used. The upper end can be formed to accommodate hand stirring or for attachment to a mechanical stirrer.

3.6 Laboratory thermometer, 0-150°C.

3.7 Titer test thermometer, see specifications in Method H10.

3.8 Filter paper, qualitative, rapid filtering grade.

3.9 Glycerol-caustic solution, prepared by dissolving with the aid of heat, 250 g. of solid potassium hydroxide in 1250 g. of glycerin (dynamite or C. P. grade). To avoid foaming, heating shall not exceed 135° to 145°C. (Sodium hydroxide can not be substituted for potassium hydroxide).

3.10 Sulfuric acid, 30% by weight sulfuric acid.

4. PROCEDURE

4.1 *Preparation of the Fatty Acids.* Approximately 110 g. of glycerol-caustic solution shall be weighed into the saponification vessel and, with stirring, heated to 150°C. Then approximately 50 ml. of oil or melted fat sample shall be added and the whole reheated to 140° to 150° C. In some cases, a little additional solution may be necessary to ensure complete saponification.

4.2 Stirring shall be continued until saponification is complete. (*Caution.* Do not heat to above 150°C.)

4.2.1 (The Committee has investigated a number of tests for complete saponification but up to the present time none has been found which is reliable under all circumstances. Familiarity with the changes which take place in the appearance and character of the mass usually enables one to determine the proper end-point. Saponification is usually indicated by a change in the appearance of the mass and often is accompanied by an increase in the viscosity, or thickening. When this occurs, the solution thins out again after the reaction is complete and assumes a homogenous appearance. The most common characteristic is that of soap bubbles forming and rising from the surface. There are cases in which none of these criteria can be depended upon so that considerable care must be exercised at all times to insure complete saponification.)

4.3 After cooling slightly, 200 to 300 ml. of distilled water shall be added and the mass stirred well and heated until the soap is dissolved. Then, with stirring, shall be carefully added 50 ml. of dilute H_2SO_4 and the whole boiled until the fatty acids are completely melted and clear. Additional water may be added before or during boiling, if desired.

4.4 The aqueous layer, containing the H_2SO_4, shall be removed, water again added and boiling repeated for 2 to 3 minutes or until the fatty acids are entirely melted and clear. Since acids of high melting point fats are sometimes slow to melt and clear, the fatty acid layer should be inspected while it is quiet to be sure all has melted.

4.5 The water again shall be removed and, if necessary, the washings described in par. 4.4 shall be repeated until the wash water is neutral to methyl orange indicator.

4.6 The fatty acids shall be transferred to a filter paper, carefully so as not to include any water. The filter paper may be supported on a small beaker without a funnel. The acids must remain completely melted until entirely filtered.

4.7 After heating the filtered acids on a hot plate to 130°C. to remove traces of moisture, the titer test tube shall be filled to a height of 57 mm. from the bottom. (*Caution.* The sample shall not be held at 130°C., or reheated to this temperature more than once. If excessive moisture is present, the water shall be allowed to settle, the fatty acids decanted and then refiltered and reheated. The acids must be thoroughly dry).

4.8 *Solidification of the Fatty Acids.* The water bath shall be adjusted to a temperature of 20° ± 1°C. for all samples having titers of 35°C. or higher, and 15° to 20°C. below the titer point for all samples with titers below 35°C.

4.9 The test tubes, containing the fatty acids, shall be placed in the water bath assembly. The titer thermometer shall be inserted to the immersion mark so that it will be equidistant from the sides of the tube. Stirring, with the stirring rod in a vertical manner, shall be done at the rate of 100 complete up and down motions per minute. (Stirring may be performed mechanically by attaching a small motor with suitable speed-reducing mechanism to the stirring rod). The stirrer shall move through a vertical distance of approximately 38 mm.; agitation being started while the temperature is at least 10°C. above the titer point.

4.10 Stirring shall continue at the directed rate until the temperature remains constant for 30 seconds, or begins to rise in less than a 30 second interval. Stirring shall be immediately discontinued, the stirrer removed or raised out of the sample, and the increase in temperature shall be observed. The titer point is the highest temperature indicated by the thermometer during this rise. Duplicate determinations shall be expected to agree within 0.2°C.

5. RESULTS

5.1 The titer point shall be expressed in degrees Fahrenheit or Centigrade.

6. HISTORY

6.1 This method has been adapted from the official methods of the American Oil Chemists Society, for fats and oils of animal, vegetable and marine origin.

A.L.C.A. Provisional Method, March 1954

CLOUD AND POUR POINT (H18)

1. SCOPE

1.1 The cloud point of a petroleum oil is the temperature at which paraffin wax or other solid substances begin to crystallize out or separate from solution when the oil is chilled under definite prescribed conditions.

1.2 The pour point of a petroleum oil is the lowest temperature at which the oil will pour or flow when it is chilled without disturbance under definite prescribed conditions.

1.3 The test for cloud point shall be used only for oils which are transparent in layers 1.5 inches thick.

1.4 The test for pour point is intended for use on any petroleum oils.

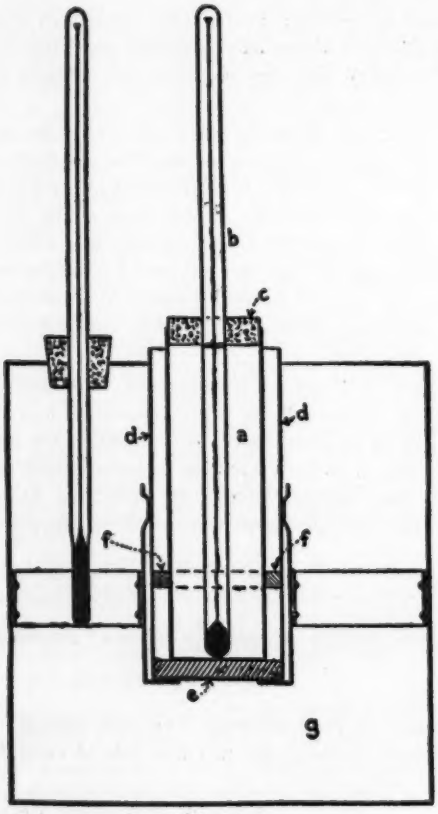


FIGURE H-18

2. SPECIMEN

2.1 The petroleum oils shall be sampled in accordance with Method J50.

3. APPARATUS

3.1 The apparatus for cloud and pour point tests shall be constructed as shown in Figure H18

3.2 The test jar, *a*, shall be of clear glass, cylindrical form, flat bottom, approximately 1 3/16 to 1 5/16 in. inside diameter, and 4.5 to 5 inches high. An ordinary 4 oz. oil sample bottle may be used if it is within the above specifications, and no test jar is available.

3.3 The thermometer, *b*, shall be one of the following. A special thermometer graduated in either Centigrade or Fahrenheit degrees, the ranges being -38° to +50°C. or -36° to +120°F., respectively. A special low cloud and pour test thermometer graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being -80° to +20° C. or -112° to +70°F., respectively. (For specifications of these thermometers, see Method H10).

3.4 The cork, *c*, shall fit the test jar, and shall be bored centrally to take the test thermometer.

3.5 The jacket, *d*, shall be of glass or metal, shall be water tight, of cylindrical form, flat bottom, about 4.5 in. deep, with inside diameter 3/8 to 1/2 in. greater than outside diameter of the test jar.

3.6 A disk of cord or cork, *e*, 0.25 in. thick and of the same diameter as the inside of the jacket will be required.

3.7 The ring gasket, *f*, shall be about 3/16 in. thick, and made to fit snugly around the outside of the test jar and loosely inside the jacket. This gasket may be made of cork, felt or other suitable material, elastic enough to cling to the test jar and hard enough to hold its shape. The purpose of the ring gasket is to prevent the test jar from touching the jacket.

3.8 The cooling bath *g*, shall be of a type suitable for obtaining the required temperatures. The size and shape of the bath are optional but a support, suitable for holding the jacket firmly in a vertical position, is essential. For determination of pour points below 50°F., two or more baths should be at hand. The required bath temperatures may be maintained by refrigeration if available, otherwise by suitable freezing mixtures, typical examples of which are

For temperatures down to 50°F., ice and water.
For temperatures down to 10°F., crushed ice and sodium chloride.
For temperatures down to -15°F., crushed ice and calcium chloride crystals.
For temperatures down to -70°F., solid carbon dioxide and acetone or gasoline.

3.8.1 The last named mixture may be made as follows: In a covered metal beaker chill a suitable amount of acetone or gasoline to 10°F., or lower, by means of an ice-salt mixture. Invert a cylinder of liquid carbon dioxide and draw off carefully into a chamois skin bag the desired amount of carbon dioxide, which through rapid evaporation will quickly become solid. Then add to the chilled acetone or gasoline enough of the solid carbon dioxide to give the desired temperature.

4. PROCEDURE

4.1 *Cloud Point.* The oil to be tested shall be brought to a temperature at least 25°F. above the approximate cloud point. Moisture, if present, shall be removed by any suitable method, as by filtration through dry filter paper until the oil is perfectly clear, but such filtration shall be made at a temperature at least 25°F. above the approximate cloud point.

4.2 The clear oil shall be poured into the test jar, *a*, to a height of not less than 2 nor more than 2.25 in. The test jar may be marked to indicate the proper level. The test jar shall be tightly closed by the cork, *c*, carrying the test thermometer, *b*, in a vertical position in the center of the jar with the thermometer bulb resting on the bottom of the jar. The disk, *e*, shall be placed in the bottom of the jacket, *d*, and the test jar with the ring gasket, *f*, 1 in. above the bottom shall be inserted into the jacket. The disk, jacket and inside of jacket shall be clean and dry.

4.3 The temperature of the cooling bath, *g*, shall be maintained at 30° to 35°F. The jacket, containing the test jar, shall be supported firmly in a vertical position in the cooling bath so that not more than 1 in. of the jacket projects out of the cooling medium. At each test thermometer reading which is a multiple of 2°F., the test jar shall be removed from the jacket, quickly but without disturbing the oil, inspected for cloud, and replaced in the jacket. This complete operation shall require not more than three seconds. If the oil does not show a cloud when it has been cooled to 50°F., the test jar shall be placed in a second bath maintained at a temperature of 0 to +5°F. If the oil does not show a cloud when it has been cooled to 20°F., the test jar shall be placed in a third bath maintained at a temperature of -30° to -25°F.

4.4 When such inspection first reveals a distinct cloudiness or haze in the oil at the bottom of the test jar, the reading of the test thermometer, corrected for error if necessary, shall be recorded as the cloud point.

4.5 *Pour Point.* The oil shall be poured into the test jar, *a*, to a height of not less than 2 nor more than 2.25 in. The jar may be marked to indicate the proper level. When necessary, the oil shall be heated in a water bath just sufficiently for pouring into the test jar. The test jar shall be tightly closed by the cork, *c*, carrying the test thermometer, *b*, in a vertical position in the center of the jar with the thermometer bulb immersed so that the beginning of the capillary shall be ⅛ in. below the surface of the oil.

4.6 Heat without stirring to a temperature of 115°F. in a bath maintained at not higher than 118°F. The oil shall then be cooled to 90°F. in air or in a water bath approximately 77°F. in temperature. Oils on which a pour point below –30°F. is expected shall be heated as above with the high cloud– and pour-test thermometer in position, cooled to 60°F. and the low cloud– and pour-test thermometer placed in position and the assembly placed in the jacket. Oils on which a pour point of above 90°F. is expected shall be heated to 115°F. or to a temperature 15°F. above the expected pour point, with the high cloud– and pour-test thermometer in position, and the test jar immediately introduced into the jacket.

4.6.1 The disk, *e*, shall be placed in the bottom of the jacket, *d*, and the test jar, with the ring gasket, *f*, 1 in. above the bottom, shall be inserted into the jacket. The disk, gasket and inside of jacket shall be clean and dry.

4.7 After the oil has cooled enough to allow the formation of paraffin wax crystals, great care shall be taken not to disturb the mass of the oil nor to permit the thermometer to shift in the oil. Any disturbance of the spongy network of wax crystals will lead to low and fictitious results.

4.8 The temperature of the cooling bath, *g*, shall be maintained at 30° to 35°F. The jacket, containing the test jar, shall be supported firmly in a vertical position in the cooling bath so that not more than 1 in. of the jacket projects out of the cooling medium.

4.9 Beginning at a temperature 20°F. before the expected pour point, at each test thermometer reading which is a multiple of 5°F., the test jar shall be removed from the jacket carefully and shall be tilted just enough to ascertain whether there is a movement of the oil in the test jar. The complete operation of removal and replacement shall require not more than 3 seconds. If the oil has not ceased to flow when its temperature has reached 50°F., the test jar shall be placed in the jacket in a second bath maintained at a temperature of 0° to +5°F. If the oil has not ceased to flow when its temperature has reached 20°F., the test jar shall be placed in the jacket in a third bath maintained at a temperature of –30° to –25°F. For determinations of very low pour points, additional baths should be maintained with successively lower temperature differentials of about 30°F. In each case the test jar shall be transferred when the temperature of the oil reaches a point 50°F. above the temperature of the new bath. At no time shall the cold test jar be placed directly in the cooling medium. As soon as the oil in the test jar does not flow when the jar is tilted, the test jar shall be held in a horizontal position for exactly 5 seconds, as noted by a stop watch or other accurate timing device and observed carefully. If the oil shows any movement under these conditions, the test jar shall be immediately replaced in the jacket and a test for flow repeated at the next temperature 5°F. lower.

4.10 The test shall be continued in this manner until a point is reached at which the oil in the test jar shows no movement when the test jar is held

in a horizontal position for exactly five seconds. Certain lubricating oils tend to move as a whole and should be very closely observed. The reading of the test thermometer at this temperature, corrected for error if necessary, shall be recorded. The pour point shall be taken as the temperature 5°F. above this solid point.

4.11 *Pour Point for Black Oils and Cylinder Stocks.* In those cases where it is known that a sample has been subjected to some temperature higher than 115°F. during the preceding 24 hours, or where the history of the sample in this respect is not known, the sample shall be held in the laboratory 24 hours before testing, unless three consecutive tests of the same sample in the same test jar give check results. For these particular oils, results obtained by one or the other of the alternative procedures shall be called the upper (maximum) pour point.

4.12 The lower (minimum) pour point shall be determined by heating a. sample with stirring to 220°F. The oil shall then be poured in the test jar, cooled to 90°F. as before, and the pour point determined as described in par 4.5.

5. RESULTS

5.1 The cloud point shall be reported in degrees Centigrade or Fahrenheit.

5.2 The pour point shall be taken as the temperature 5°F. above the solid point, and shall be reported in degrees Centigrade or Fahrenheit.

5.3 Upper and lower pour points shall be reported separately for black oils and cylinder stocks and shall be expressed in degrees Centigrade or Fahrenheit.

6. HISTORY

6.1 This method is A.S.T.M. Designation D 97-47 and is published by permission of American Society for Testing Materials.

A.L.C.A. Provisional Method, March 1954

MOISTURE AND VOLATILE MATTER (H20)

1. SCOPE

1.1 This method determines the moisture and other material volatile under conditions of the test. It is applicable to all the ordinary fats and oils, including emulsions. It is not applicable to certain abnormal samples such as solvent extracted fats and oils which may contain residues from solvents with fairly high melting points.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

2.2 Since water tends to settle in samples which have softened or melted, care must be taken to mix samples thoroughly in order to distribute the water uniformly. The specimen shall be softened, if necessary, with gentle heat (but not melted) and mixed with an efficient mixer.

3. APPARATUS

3.1 Electric hot plate. Surface should have a high polish, otherwise cover with an asbestos pad to prevent wear on the moisture dish.

3.2 Glass beakers, 100 to 150 ml.

3.3 Desiccator containing an efficient desiccant. Calcium chloride is not satisfactory. (See Method H10 for specifications for desiccants.).

4. PROCEDURE

4.1 Five to 20 g. of a well mixed sample shall be accurately weighed into a tared beaker which has been previously dried and cooled in a desiccator. The sample shall then be heated on the hot plate, rotating the beaker gently, by hand, to avoid spattering which may result from too rapid ebullition of moisture.

4.2 The approach of the end-point may be judged by the cessation of the rising bubbles of steam as well as by the absence of foam. Another good method of judging the end-point is to place a clean, dry watch glass on top of the beaker. The evolution of steam is indicated by condensation on the watch glass. The temperature of the sample shall at no time be allowed to exceed 130°C., except at the end of test.

4.3 When the apparent end-point has been reached, the sample shall be heated momentarily to the point of incipient smoking, using caution not to overheat, and then cooled to room temperature in a desiccator and weighed.

5. RESULTS

5.1 The moisture and volatile matter shall be reported in per cent, by weight, employing the calculation

$$\text{Per cent moisture and volatile matter} = \frac{\text{Loss in Weight x 100}}{\text{Weight of Sample}}$$

6. HISTORY

6.1 This method has been adapted from the official methods of the American Oil Chemists Society, for fats and oils of animal, vegetable and marine origin.

A.L.C.A. Provisional Method, March 1954

INSOLUBLE IMPURITIES (H21)

1. SCOPE

1.1 This method determines the dirt, meal and other foreign substances insoluble in kerosene and petroleum ether and is applicable to all normal fats and oils.

2. SPECIMEN

2.1 Samples shall be taken in accordance with Method J50. The specimen shall be softened, if necessary, with gentle heat (but not melted) and mixed with an efficient mixer.

3. APPARATUS AND REAGENTS

3.1 Gooch crucible, prepared with a pad of acid-washed asbestos, approximately 2 mm. thick. The pad shall be washed with water, alcohol, and ether. The crucible shall be dried to constant weight at 101° ± 1°C., cooled in a desiccator to room temperature and weighed.

3.2 Filter-flask of convenient size and Gooch crucible adapter.

3.3 Petroleum ether, having specifications in accordance with Method H10.

3.4 Kerosene, refined petroleum distillate with a flash point not below 23°C. (75°F.) as determined by the A.S.T.M. Standard Method D56 using the Tag Closed Tester. The kerosine shall be filtered through a Gooch crucible, prepared as in par. 3.1, before using.

4. PROCEDURE

4.1 The residue from the Moisture and Volatile determination (Method H20) shall be used or a sample prepared in the same manner.

4.2 To the residue shall be added 50 ml. of kerosene and, after heating on a water bath to dissolve the fat, filter through the prepared Gooch crucible with the aid of a vacuum. The contents of the crucible shall be washed with five 10 ml. portions of hot kerosene, allowing each portion to drain before adding the next.

4.3 The residue in the crucible shall then be washed thoroughly with petroleum ether to remove all of the kerosene. (Carbon tetrachloride, A.C.S. grade may be employed instead of petroleum ether). The crucible and contents shall be dried to constant weight at 101° ± 1°C., cooled to room temperature in a desiccator and weighed.

5. RESULTS

5.1 The calculation of insoluble impurities is reported as percentage

$$\text{Per cent insoluble impurities} = \frac{\text{Gain in weight of crucible} \times 100}{\text{Weight of sample taken for moisture}}$$

6. HISTORY

6.1 The method has been adapted from the official methods of the American Oil Chemists Society for fats and oils of animal, vegetable and marine origin.

A.L.C.A. Provisional Method, March 1954

ASH (H22)

1. SCOPE

1.1 This method determines the residue remaining after incineration under the specific conditions of the test and is applicable to animal fats and vegetable and marine oils.

2. SPECIMEN

2.1 Samples shall be taken in accordance with Method J50. The specimen shall be softened, if necessary, with gentle heat (but not melted) and mixed with an efficient mixer.

3. APPARATUS

3.1 Platinum dish, 100 ml. capacity.

4. PROCEDURE

4.1 The platinum dish shall be heated to redness, cooled slightly and, after placing in a desiccator and cooling to room temperature, shall be weighed.

4.2 A sample of 50 ± 0.1 g. in the platinum dish shall be heated gently on a burner until the sample can be ignited at the surface. The size of the flame shall be then reduced until the heat is just sufficient to keep the sample burning. When sufficient sample has burnt to permit the addition of more, the heat source shall be removed and the dish allowed to cool until the fat ceases burning. A second weighed portion of the sample shall then be added so that a total of about 75 g. is used.

4.3 Heating shall be continued until the sample is a black char whereupon the dish is transferred to an electric muffle furnace and heated at 550° to 650° C. for one hour.

4.4 After removing from the furnace and cooling slightly, the dish shall be placed in a desiccator, cooled to room temperature and weighed. Heating in the furnace shall be repeated until the ash reaches constant weight.

5. RESULTS

5.1 The ash shall be calculated according to the following formula and the results reported in per cent, by weight

$$\text{Per cent ash} = \frac{\text{Weight of residue x 100}}{\text{Weight of sample}}$$

6. HISTORY

6.1 This method has been adapted from the official methods of the American Oil Chemists Society, for fats and oils of animal, vegetable and marine origin.

A.L.C.A. Provisional Method, March 1954

SEDIMENT IN MOELLON (H23)

1. SCOPE

1.1 This test is intended to determine the amount of sediment in the sample insoluble in industrial 90 benzene or technical benzol.

2. SPECIMEN

2.1 The moellon shall be sampled in accordance with Method J50.

3. APPARATUS

3.1 The extraction apparatus shall consist of an extraction flask, condenser and extraction thimble.

3.1.1 Extraction flask. An Erlenmeyer flask of 1-liter capacity or a wide mouth Erlenmeyer flask approximately 500 ml. capacity.

3.1.2 Condenser. Underwriter's form, comprising a block tin coil approximately 1 inch in diameter and 2 inches in length, attached to and with the ends projecting through a lid of sufficient diameter to cover the neck of the flask.

3.1.3 Extraction thimble. An alundum (porous grade) thimble (1 inch in diameter by 2.75 inches in height, weighing not less than 15 or more than 17 g.). The thimble shall be suspended by means of a platinum wire so that it hangs approximately 1.75 inches above the extracting solvent and 1.75 inches below the condenser coil. (Alundum thimble No. 5163 RA 98 from Norton Co., Worcester, Mass. is satisfatory).

4. PROCEDURE

4.1 The thimble shall be given a preliminary extraction before use, allowing solvent to drip from thimble for at least one hour. Then it shall be dried for 1 hour at 105° to 110°C., cooled and weighed to the nearest 0.0001 g. The extraction shall be repeated until the weight of the thimble, after two successive extractions does not differ by more than 0.0002 g.

4.2 Approximately 10 g. of moellon shall be placed in the thimble and weighed to the nearest 0.01 g. After placing the thimble in the extraction

apparatus, it shall be extracted with industrial 90 benzene or technical benzol until the solvent dropping from the thimble is colorless. The rate of extraction shall be such that the surface of oil and benzol in thimble does not rise higher than to within ¾ in. of top.

4.3 After completion of the extraction, the thimble shall be dried for 1 hour at 105° to 110°C., cooled and weighed to the nearest 0.0001 g. The extraction shall be repeated for a period of one hour, but no longer than 1.25 hours, and then shall be dried, cooled and weighed as before. The extraction shall be repeated, if necessary, until the weight of thimble and sediment does not differ by more than 0.001 g.

5. RESULTS

5.1 The sediment in the moellon shall be reported in per cent, by weight.

6. HISTORY

6.1 This method is a modification of A.S.T.M. Designation: D 473-48 and Method 300.2.2 of Federal Specification VV-L-791d.

A.L.C.A. Provisional Method, March 1954

FREE FATTY ACIDS (H30)

1. SCOPE

1.1 This method is intended to determine the free fatty acids existing in the sample and is applicable to crude and refined vegetable and marine oils and animal fats.

2. SPECIMEN

2.1 The sample shall be taken as described in Method J50.

3. APPARATUS AND REAGENTS

3.1 Oil sample bottles, 115 or 230 ml. (4 or 8 oz.) or 250 ml. Erlenmeyer flasks.

3.2 Ethyl alchol, 95 per cent (U.S.S.D. Formulas 30 and 3A shall be permitted). The alcohol shall give a definite, distinct and sharp end-point with phenolphthalein and shall be neutralized with alkali to a faint but permanent pink color just before using. (Isopropanol, 99 per cent, may be used as an alternate solvent with crude and refined vegetable oils).

3.3 Phenolphthalein indicator solution, 1 per cent in 95 per cent alcohol.

3.4 Sodium hydroxide solution, accurately standardized.

4. PROCEDURE

4.1 The following table shall be used to determine the quantities to be used with various ranges of fatty acids.

Free Fatty Acid Range (%)	Grams of Sample	Milliliters of Alcohol	Normality of Alkali
0.0 to 0.2	56.4 ±0.2	50	0.1
0.2 to 1.0	28.2 ±0.2	50	0.1
1.0 to 30.0	7.05 ±0.05	75	0.25
30.0 to 50.0	7.05 ±0.05	100	0.25 or 1.0
50.0 to 100.0	3.525±0.001	100	1.0

4.2 The sample shall be entirely liquid and well mixed before weighing. Then the designated sample size shall be weighed into an oil-sample bottle or Erlenmeyer flask to which is added the specified amount of hot, neutralized alcohol and 2 ml. of indicator.

4.3 Shaking vigorously, the titration with alkali shall be made to the appearance of the first permanent pink color of the same intensity as that of the neutralized alcohol before addition of the sample. The color shall persist for 30 seconds.

5. RESULTS

5.1 The free fatty acids shall be reported in per cent, by weight.

$$\text{Per cent free fatty acids} = \frac{\text{Ml. of alkali x N x 28.2}}{\text{Weight of sample}}$$

5.2 The free fatty acids are frequently expressed in terms of acid value instead of per cent free fatty acids. The acid value is defined as the number of mg. of KOH necessary to neutralize 1 g. of sample. To convert per cent free fatty acids (as oleic) to acid value, the former is multiplied by 1.99.

6. HISTORY

6.1 This method has been adapted from the official methods of the American Oil Chemists Society, for fats and oils of animal, vegetable and marine origin.

A.L.C.A. Provisional Method, March 1954

SAPONIFICATION VALUE (H31)

1. SCOPE

1.1 This method is intended to determine the saponification value of all normal fats and oils.

1.2 The saponification value is defined as the amount of alkali necessary to saponify a definite quantity of the sample and is expressed as the number of milligrams of potassium hydroxide required to saponify 1 gram of sample.

2. SPECIMEN

2.1 The sample shall be taken as described in Method J50.

3. APPARATUS AND REAGENTS

3.1 Erlenmeyer flasks, Corning Alkali Resistant, Kimble Resistant or equivalent, 250 or 300 ml.

3.2 Air condensers, minimum length 650 mm.

3.3 Water bath or a hot plate with variable heat control.

3.4 Hydrochloric acid, 0.5 *N*, accurately standardized.

3.5 Alcoholic potassium hydroxide. To a 2 liter flask shall be added from 1 to 1.5 liters of 95 per cent ethyl alcohol (U.S.S.D. Formulas 20 and 3A are permitted) and a few grams (5 to 10 g.) of potassium hydroxide. After boiling under a reflux condenser on a water bath for 30 to 60 minutes, the alcohol shall be distilled and collected. For the preparation of alcoholic potassium hydroxide, 40 g. of potassium hydroxide, low in carbonate, shall be dissolved in 1 liter of the distilled alcohol, keeping the temperature below 15.5°C. (60°F.) while the alkali is being dissolved. This solution should remain clear.

4. PROCEDURE

4.1 The sample, if not already liquid, shall be melted and filtered through filter paper to remove any impurities and the last traces of moisture. The sample must be completely dry.

4.2 A sample, of such size (usually 4 to 5 g.) that the back titration is 45 to 55 per cent of the blank, shall be weighed accurately and 50 ml. of the alcoholic KOH is added with a pipette, allowing the pipette to drain for a definite period of time.

4.2.1 A blank determination shall be prepared and conducted simultaneously with the sample.

4.3 Air condensers shall be connected to the flask and the solution boiled gently but steadily until the sample is completely saponified. This usually requires approximately 30 minutes for normal samples. Care shall be taken that the vapor ring in the condenser does not rise to the top of the condenser or there may be some loss.

4.4 After the flask and condenser have cooled somewhat, but not sufficient to jell the contents, the inside of the condenser shall be washed down with a little distilled water. The flask is then disconnected, approximately 1 ml. of indicator added and the solution shall be titrated with 0.5 *N* HCl until the pink color has just disappeared.

5. RESULTS

5.1 The saponification number shall be calculated as follows:

$$\text{Saponification value} = \frac{28.05\ (A - B)}{\text{Weight of Sample}}$$

where A = titration of blank
B = titration of sample

6. HISTORY

6.1 This method has been adapted from the official methods of the American Oil Chemists Society, for fats and oils of animal, vegetable and marine origin.

A.L.C.A. Provisional Method, March 1954

IODINE VALUE — WIJS METHOD (H32)

1. SCOPE

1.1 This method is intended to determine the iodine value of all normal fats and oils not containing conjugated systems.

1.2 The iodine value is a measure of the unsaturation of fats and oils and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 Glass stoppered bottles or wide mouth Erlenmeyer flasks, 500 ml. Wide mouth bottles or flasks are essential if stirring is done by mechanical means.

3.2 Glass stoppered volumetric flasks, conforming to Bureau of Standards tolerances and accurately calibrated to contain 1000 ml.

3.3 Pipette, 20 ml.

3.4 Two pipettes, 25 ml. One pipette is reserved for use with the standard potassium dichromate solution and shall conform to Bureau of Standard tolerances and be calibrated to deliver 25 ml.

3.5 Glacial acetic acid, A.C.S. grade. The permanganate test shall be applied to be sure that this specification is met.

3.5.1 Two milliliters of the glacial acetic acid shall be diluted with 10 ml. of distilled water and 0.1 ml. of 0.1 *N* $KMnO_4$ shall be added. The pink color must not be entirely discharged within 2 hours.

3.6 Potassium iodide, A.C.S. grade.

3.7 Chlorine, 99.8 per cent. Satisfactory commercial grades are available in cylinders, but this gas must be dried by passing through sulfuric acid (sp. gr. 1.84) before introducing into the iodine solution.

3.7.1 Chlorine may be prepared by allowing hydrochloric acid (sp. gr. 1.19) to drop onto potassium permanganate or on a mixture of potassium permanganate and manganese dioxide. The gas thus generated shall be led through a glass tube into sulfuric acid (sp. gr. 1.84) and then into the iodine solution.

3.8 Carbon tetrachloride, A.C.S. grade.

3.9 Hydrochloric acid, A.C.S. grade, sp. gr. 1.19.

3.10 Soluble starch, of suitable sensitivity.

3.10.1 The test for starch sensitivity shall be made by adding, while stirring, 200 ml. of boiling water to a paste made with 1 g. of starch in a small amount of water. After placing 5 ml. of this solution in 100 ml. of water, add 0.05 ml. of 0.1 *N* iodine solution. The deep blue color produced must be discharged by 0.05 ml. of 0.1 *N* sodium thiosulfate.

3.11 Potassium dichromate, A.C.S. grade, shall be finely ground and dried to constant weight at about 110°C. before using. (A standard sample of potassium dichromate with a certificate of analysis may be obtained from the National Bureau of Standards at Washington, D. C. This sample is strongly recommended as the primary standard for this method. The dichromate should be treated as directed in the certificate of analysis accompanying the sample).

3.12 Sodium thiosulfate ($Na_2S_2O_3.5H_2O$), A.C.S. grade.

3.13 Iodine, A.C.S. grade.

3.14 Potassium iodide solution, prepared by dissolving 150 g. in distilled water and making up to 1 liter.

3.15 Starch indicator solution, shall be prepared by making a homogeneous paste of 10 g. of soluble starch in cold distilled water and adding to this 1 liter of boiling distilled water with rapid stirring. Cool. Salicylic acid (1.25 g. per liter) shall be added to preserve the indicator. If long storage is required, the solution shall be kept in a refrigerator at 4° to 10°C. (40° – 50°F.). Fresh indicator shall be prepared when the end-point of the titration from blue to colorless fails to be sharp.

3.16 Standard potassium dichromate solution, 0.1 *N*, shall be prepared by dissolving 4.9035 g. of finely ground and dried potassium dichromate in distilled water in the 1000 ml. volumetric flask and making to volume at 25°C.

3.17 Sodium thiosulfate solution, 0.1 *N*, prepared by dissolving 24.8 g. of sodium thiosulfate in distilled water and diluting to 1 liter.

3.17.1 Standardization of the thiosulfate shall be accomplished as follows: Pipette 25 ml. of the standard dichromate solution into Erlenmeyer flask or bottle. Add 5 ml. of hydrochloric acid, 10 ml. of potassium iodide solution and rotate to mix. Allow to stand for 5 minutes and then add 100 ml. of distilled water. Titrate with sodium thiosulfate solution, shaking continuously, until the yellow color has almost disappeared. Add 1 to 2 ml. of indicator and continue titration adding the thiosulfate solution slowly, until the blue color has just disappeared. The strength of the sodium thiosulfate solution is expressed in terms of its normality.

$$\text{Normality of } Na_2S_2O_3 \text{ solution} = \frac{2.5}{\text{Ml. } Na_2S_2O_3 \text{ soln. required}}$$

3.18 Wijs solution, prepared by dissolving 13.0 g. of iodine in 1 liter of glacial acetic acid. Gentle heat may be necessary to promote solution. Cool and remove a small quantity (100 to 200 ml.) and set aside in a cool place for future use. Pass dry chlorine gas into the iodine solution until the original titration is not quite doubled. A characteristic color change takes place in the Wijs solution when the desired amount of chlorine has been added. This may be used to assist in judging the end point. A convenient procedure is to add a small excess of chlorine and bring back to the desired titration by addition of some of the original iodine solution which was taken out at the beginning. The original iodine solution and the finished Wijs solution shall be both titrated with $Na_2S_2O_3$ solution as directed in par. 4.6.

4. PROCEDURE

4.1 The sample, if not already completely liquid, shall be melted and filtered through filter paper to remove any impurities and the last traces of water. (Care must be taken not to exceed 10° to 15° C. above the sample melting point during melting and filtering). The sample must be absolutely dry.

4.2 The sample shall be accurately weighed into a 500 ml. flask or bottle to which have been added 20 ml. of CCl_4. The weight of sample must be such that there will be an excess of Wijs solution of 50 to 60 per cent of the amount added, i. e. 100 to 150 per cent of the amount absorbed. The following table is a convenient guide for selecting the size of sample.

Iodine Value	Sample Weight, Grams		Weighing Accuracy, Grams
	100% Excess	150% Excess	
Less than 3	10	10	±0.001
3	10.5760	8.4613	0.005
5	6.3460	5.0770	0.0005
10	3.1730	2.5384	0.0002
20	1.5865	0.8461	0.0002
40	0.7935	0.6346	0.0002
60	0.5288	0.4231	0.0002
80	0.3966	0.3173	0.0001
100	0.3173	0.2538	0.0001
120	0.2644	0.2115	0.0001
140	0.2266	0.1813	0.0001
160	0.1983	0.1587	0.0001
180	0.1762	0.1410	0.0001
200	0.1586	0.1269	0.0001

4.3 Twenty-five (25) ml. of the Wijs solution shall be pipetted into the flask containing the sample and swirled to insure an intimate mixture.

4.4 At least 2 blank determinations shall be prepared and conducted with each group of samples simultaneously and similar in all respects.

4.5 The flasks shall be stored in a dark place for 30 minutes at a temperature of 25° ± 5°C. (Samples with an iodine value above 150, such as linseed and perilla oils, shall be stored for 1 hour).

4.6 From storage, the flasks shall be removed and 20 ml. of KI solution added followed by 100 ml. of distilled water. The solution shall be titrated with 0.1 *N* $Na_2S_2O_3$ solution, adding gradually and with constant shaking. (Mechanical stirring is very satisfactory for agitating during the addition of thiosulfate). The titration shall be continued until the yellow color has almost disappeared, 1 to 2 ml. of starch indicator solution is added and the titration shall be continued until the blue color has just disappeared.

5. RESULTS

5.1 The iodine value shall be calculated as follows:

$$\text{Iodine value} = \frac{(B - S) \times N \times 12.69}{\text{Weight of sample}}$$

where B = titration of blank
S = titration of sample
N = normality of $Na_2S_2O_3$ solution

6. HISTORY

6.1 This method has been adapted from the official methods of the American Oil Chemists Society, for fats and oils of animal, vegetable and marine origin.

A.L.C.A Provisional Method, March 1954

MOISTURE (H40)

1. SCOPE

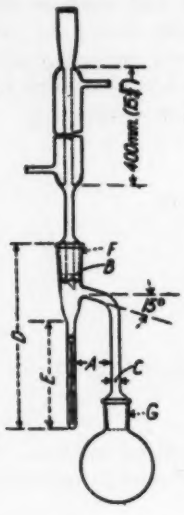
1.1 This method of analysis determines water existing in a sample of sulfonated or sulfated oil, or both, by distilling the sample with a volatile solvent. In addition to normal fats and oils, the method is applicable to sulfonated and sulfated oils that do not contain the following: mineral acids, free sulfonic acids, or free sulfuric acid esters; or alkali hydroxides, carbonates, or acetates; or alcohol, glycerol, diethylene glycol, acetone, or other water miscible volatile compounds.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 The apparatus required consists of a glass flask heated by suitable means and provided with a reflux condenser discharging into a trap and connected to the flask. The connections between the trap and the condenser and flask shall be interchangeable ground joints. The trap serves to collect and measure the condensed water and to return the solvent to the flask. A suitable assembly of the apparatus is illustrated in Figure H40.



A = 45 to 55 mm.
B = 22 to 24 mm. in inside diameter
C = 9 to 11 mm. in inside diameter
D = 235 to 240 mm.
E = 146 to 156 mm.
F and G are interchangeable joints, standard taper 24/40.

FIGURE H-40

3.1.1 Flask. A 500 ml. flask of either the short-neck round-bottom type or the Erlenmeyer type shall be used.

3.1.2 Heat Source. The source of heat may be either an oil bath (stearic acid, paraffin wax, etc.), or an electric heater provided with a sliding rheostat or other means of heat control.

3.1.3 Condenser. A water-cooled glass reflux condenser (Figure H40), having a jacket approximately 400 mm. (15 ¾ in.) in length with an inner tube 9.5 to 12.7 mm. (⅜ to ½ in.) in outside diameter shall be used. The end of the condenser to be inserted in the trap shall be ground off at an angle of 30° from the vertical axis of the condenser. When inserted into the trap, the tip of the condenser shall be about 7 mm. (¼ in.) above the surface of the liquid in the trap after the distillation conditions have been established. Figure H40 shows a conventional sealed-in type of condenser, but any other condenser fulfilling the detailed requirements above may be used.

3.1.4 Trap. A trap made of well annealed glass constructed in accordance with Figure H40 and graduated as shown to contain 5 ml. at 20°C. shall be used. It shall be subdivided into 0.1 ml. divisions, with each 1 ml. line numbered (5 ml. at top). The error in any indicated capacity may not be greater than 0.05 ml.

3.2 Xylene, c. p.

3.3 Oleic Acid. Oleic Acid, U.S.P. grade, heated previous to use for 5 to 10 min. over a free flame to a temperature of 130° to 135°C.

4. CALIBRATION

4.1 To calibrate the apparatus add approximately 1 g. of water to a mixture of 80 g. of xylene and 10 g. of oleic acid. Conduct the distillation as described in par. 5.2, 5.3 and 5.4. When all the water has distilled, cool the apparatus, add another gram of water, and repeat the distillation. Continue the calibration up to the capacity of the receiving tube.

5. PROCEDURE

5.1 Before using, clean the condenser and the receiving tube thoroughly with soap and warm water, rinse well, then treat with hot cleaning solution [a mixture of 10 ml. of saturated $K_2Cr_2O_7$ and 990 ml. of H_2SO_4 (sp. gr. 1.84)] and finally thoroughly wash and dry.

5.2 Take enough of the sample to be tested for analysis to yield about 4 ml. of water. Introduce the approximate quantity into a weighing bottle and make the weighings from the bottle into the flask, taking care that after removal of the sample no drops of oil are left on the outside of the weighing bottle. Add 80 g. of xylene and oleic acid equivalent to about two and one-half times the weight of the bone-dry sample to prevent foaming and jellying of the contents of the flask. Introduce glass beads to prevent bumping and mix the contents of the flask thoroughly by swirling, care being taken to avoid any loss of material. Fill the trap with xylene and immediately connect the flask with the distillation apparatus. Insert a loose cotton plug in the top of the condenser tube to prevent condensation of atmospheric moisture in the condenser tube.

5.3 Heat the flask and regulate the heating so that the condenser tube immediately below the water jacket is just barely hot. In this way a minimum of water will condense further up the condenser where it may be difficult to volatilize any moisture condensed on the walls.

5.4 Continue the distillation at the specified rate until practically no water is visible on any part of the apparatus except within the graduations of the trap. This operation usually requires less than an hour. Increase the rate of distillation in order to remove all traces of condensed water in the condenser tube and continue the distillation until the water level in the trap remains unchanged after a 10 min. interval. Dislodge any droplets adhering to the

side of the receiver with a thin copper wire twisted into a loop. Immerse the receiving tube in warm water at about 40°C. for 15 min. or until the xylene layer becomes clear, then read and record the temperature and the exact volume of the water in the trap.

6. RESULTS

6.1 The volume of condensed water measured in the trap may be converted into its equivalent weight in grams by means of following table

Specific Gravity of Water*

Temperature deg. Cent.	Specific Gravity
4	1.00000
35	0.99406
36	0.99371
37	0.99336
38	0.99299
39	0.99262
40	0.99224
41	0.99186
42	0.99147
43	0.99107
44	0.99066
45	0.99025

* This table is taken from Smithsonian Tables, compiled from various authors.

6.2 Calculate the percentage of water as follows:

$$\text{Water, per cent} = \frac{\text{wt. of water in grams}}{\text{wt. of sample in grams}} \times 100$$

7. HISTORY

7.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500–45) of the American Society for Testing Materials, and is published by their permission.

A.L.C.A. Provisional Method, March 1954

MOISTURE AND VOLATILE MATTER (H41)

1. SCOPE

1.1 This method of analysis determines the percentage of water and other compounds volatile at about 100°C. existing in a sample of sulfonated or sulfated oil, or both, by rapid evaporation. The method is applicable only to sulfonated and sulfated oils that do not contain the following: mineral

acids, free sulfonic acids or free sulfuric acid esters, ammonia, acetic acid or similar volatile acids, alkali hydroxides, carbonates, acetates or similar salts which may react with oleic acid at elevated temperatures liberating volatile acids, or glycerol, diethylene glycol, xylene, or other compounds of similar volaltility.

2. SPECIMEN

2.1 The sample shall be taken as described in Method J50.

3. APPARATUS AND REAGENTS

3.1 The apparatus required consists of a glass-stoppered weighing flask, a glass beaker and a suitable thermometer.

3.1.1 Weighing Flask. Any suitable glass-stoppered weighing flask of 10 to 15 ml. capacity may be used.

3.1.2 Beaker. A Griffin low-form glass beaker with an approximate capacity of 150 ml. and a diameter of about 5 cm. shall be used.

3.1.3 Heat Source. The source of heat may be either an electric hot plate with or without asbestos paper or board cover, or an open flame under a suitable asbestos board and a wire gauze (to spread the heat).

3.1.4 Thermometer. A thermometer graduated from 90° to 150°C., about 3 in. in length, and substantially constructed shall be used.

3.2 Oleic Acid, U.S.P.

3.3 Desiccating Agent. Any suitable desiccating agent may be used. (See Method H10 for specifications for desiccants.)

4. PROCEDURE

4.1 Weigh approximately 5 g. of oleic acid into the beaker and insert the thermometer. Heat the oleic acid gradually, while stirring with the thermometer, until the temperature reaches 130°C. Place the beaker in an oven at 105° to 110°C. for 15 min., cool in a desiccator and weigh. Repeat the heating over the hot plate and in the oven until two successive weighings differ by less than 1.5 mg.

4.2 Place about 6 g. of the sample in the weighing flask and determine the weight accurately. Transfer the sample to the beaker (containing the oleic acid and the thermometer) and weigh the flask again. Heat the mixture exactly as in the taring of the beaker as described in par. 4.1. The loss in weight is equivalent to the moisture in the sample.

5. RESULTS

5.1 Calculate the percentage of moisture and volatile matter in the sample as follows:

$$\text{Moisture and volatile matter (hot plate test), per cent} = \frac{\text{loss of wt. in grams} \times 100}{\text{wt. of sample in grams}}$$

6. HISTORY

6.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated Oils (A.S.T.M. Designation: D 500–45) of the American Society for Testing Materials, and is published with their permission.

A.L.C.A. Provisional Method, March 1954

ORGANICALLY COMBINED SULFURIC ANHYDRIDE (H42)

TITRATION TEST (FOR SULFATED OILS)

1. SCOPE

1.1 This method of analysis determines the organically combined sulfuric anhydride existing in a sample of sulfated oil by boiling the sample with sulfuric acid and determining the acidity of the reaction mixture. This method is applicable only to oils that split off their combined SO_3 upon boiling with mineral acids and that do not contain compounds which cannot be accurately titrated in water solution with methyl orange as the indicator.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

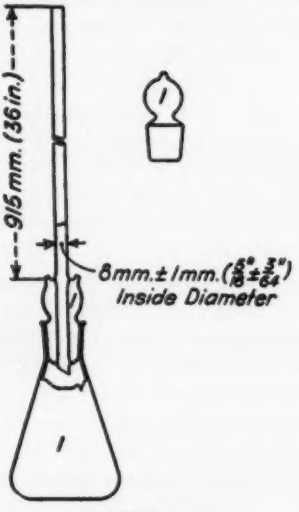


FIGURE H-42

3. APPARATUS AND REAGENTS

3.1 The apparatus required consists of a glass flask provided with a glass stopper and an air condenser. The connection between the flask and the condenser shall be a ground joint. Perforated glass beads shall be used to prevent bumping.

3.1.1 Flask. An Erlenmeyer flask made of heat-resistant glass, such as Pyrex, having a capacity of approximately 300 ml. and provided with a glass stopper shall be used.

3.1.2 Condenser. The condenser required consists of a glass tube, 915 mm. (36 in.) in length, and 8 mm. ($^5/_{16}$ in.) in outside diameter. The lower end of the tube shall be flared and ground to fit the mouth of the Erlenmeyer flask.

3.1.3 Glass Beads. Perforated glass beads, made of chemically-resistant glass, approximately 4 mm. ($^5/_{32}$ in.) in diameter shall be used. Before using, the glass beads shall be boiled thoroughly in several portions of water or until the wash water reacts neutral to methyl orange indicator.

3.2 Sodium Hydroxide (1.0 *N*). Accurately standardize a 1.0*N* NaOH solution. Express the strength or concentration of the solution as milligrams of KOH per milliliter; 1 ml. of 1.0 *N* NaOH is equivalent to 56.1 mg. of KOH.

3.3 Sodium Hydroxide (0.5 *N*). Accurately standardize a 0.5 *N* NaOH solution. Express the strength of the solution as milligrams of KOH per milliliter; 1 ml. of 0.5 *N* NaOH is equivalent to 28.05 mg. of KOH.

3.4 Sulfuric Acid (Approximately 1.0 *N*).

3.5 Sulfuric Acid (0.5 *N*). Accurately standardize a 0.5 *N* H_2SO_4 solution. Express the strength of the solution as milligrams of KOH per milliliter; 1 ml. of 0.5 *N* H_2SO_4 is equivalent to 28.05 mg. of KOH.

3.6 Ethyl Ether, U.S.P.

3.7 Sodium Chloride. Solid, c. p. NaCl.

3.8 Methyl Orange (0.1 per cent). Prepare a 0.1 per cent water solution of methyl orange indicator.

4. PROCEDURE

4.1 The procedure consists of two determinations: namely, (*a*) the alkalinity of the sample, designated as A, and (*b*) the increase in acidity after boiling the sample with sulfuric acid, designated as F.

4.2 *Alkalinity, A.* Dissolve 10 g. of the sample in 100 ml. of water in the 300 ml. glass-stoppered Erlenmeyer flask, warming to obtain solution if necessary. After cooling, add 30 g. of NaCl, 25 ml. of ether, and five drops of methyl orange indicator, then add 0.5 *N* H_2SO_4 with frequent but gentle shaking until the mixture is slightly acid. Shake the contents of the flask vigorously, and complete the titration by adding first 0.5 *N* NaOH several drops at a time until the solution is alkaline and then the acid one or two drops at a time until the end point is reached. Shake the solution vigorously after

each addition of reagent. Drain burettes for 3 min. before readings are taken. Calculate the alkalinity, A, as follows:

$$A = \frac{(B \times D) - (C \times E)}{W}$$

where:

A = total alkalinity in milligrams of KOH per gram,
B = milliliters of acid,
C = milliliters of alkali,
D = strength of the acid in milligrams of KOH per milliliter,
E = strength of the alkali in milligrams of KOH per milliliter, and
W = weight of the sample in grams.

4.3 *Increase in Acidity upon Boiling, F.* Weigh 10 g. of the sample into the Erlenmeyer flask and boil under the air condenser with 1.0 *N* H_2SO_4 for 1.5 hours or until both the oil and water layers are perfectly clear, using glass beads to prevent bumping. The volume of H_2SO_4 added shall be sufficient to neutralize the total alkalinity, A, of the sample plus 25 ml. in excess. Regulate the heating so that the solution boils rather vigorously but with very little evaporation taking place. At the end of the heating period allow the contents to cool, wash the condenser with a spray of water from a wash bottle and disconnect the condenser. Add 30 g. of NaCl, 25 ml. of ether, 50 ml. of water, and five drops of indicator and titrate the solution with 1.0 *N* NaOH to the same end point as in the total alkalinity titration in par. 4.2. During the titration stopper the flask frequently and shake the contents of the flask thoroughly. Drain the burettes for 3 min. before readings are taken.

4.3.1 Reserve the titrated solution for the subsequent determination of total desulfated fatty matter in Method H45.

4.3.2 Make a blank determination simultaneously with the sample, using the same amount and strength of the H_2SO_4, approximately the same weight of glass beads, and heating and titrating under the same conditions, as the sample. Calculate the increase in acidity upon boiling, F, as follows:

$$F = \frac{(S - B)\,N}{W}$$

where:

F = increase in acidity upon boiling in milligrams of KOH per gram,
S = milliliters of NaOH necessary to titrate the sample,
B = milliliters of NaOH necessary to titrate the blank,
N = strength of the NaOH expressed as milligrams of KOH per milliliter, and
W = weight of the sample in grams.

4.3.3 The increase in acidity, F, may be negative, in which case retain the sign obtained from the above formula in the calculation in par. 5.1.

5. RESULTS

5.1 Calculate the percentage of organically combined sulfuric anhydride as follows:

Organically combined sulfuric anhydride, per cent $= 0.1426\ (A + F)$

where:

0.1426 = one-tenth of the molecular ratio of SO_3 : KOH,
A = total alkalinity in milligrams of KOH per gram, and
F = increase in acidity upon boiling, expressed as milligrams of KOH per gram. Retain the sign of F as obtained in par. 4.3.2.

6. HISTORY

6.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45) of the American Society for Testing Materials, and is published with their permission.

A.L.C.A. Provisional Method, March 1954

ORGANICALLY COMBINED SULFURIC ANHYDRIDE (H43)

EXTRACTION-TITRATION TEST (FOR SULFATED OILS)

1. SCOPE

1.1 This method of analysis determines the organically combined sulfuric anhydride existing in a sample of sulfated oil by extracting the undecomposed sulfated fat and other fatty matter over an acidulated, concentrated salt solution, boiling the residue with sulfuric acid after evaporating the solvent, and titrating the products of reaction. This method is applicable only to sulfated oils that split off their combined SO_3 upon boiling with mineral acids, including samples containing sodium acetate or other compounds that cannot be accurately titrated in water solution with methyl orange as the indicator.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 The apparatus shall be the same as described for Method H42, par. 3.

3.2 The solutions shall be the same as described for Method H42, par. 3.2 through 3.8.

4. PROCEDURE

4.1 The procedure consists of isolating and purifying the fatty matter as it exists in the original oil by dissolving the sample in a solvent, acidifying and washing with saturated brine, and determining the increase in acidity upon boiling the isolated product with sulfuric acid. This increase in acidity is designated as F.

4.2 *Separation of Purified Oil.* Weigh 5 to 10 g. of the sample, depending upon the concentration of the fatty matter, into a 250 ml. separatory funnel containing 50 ml. of concentrated NaCl solution, some solid NaCl, 5 drops of methyl orange indicator, and 50 ml. of ether. Shake the mixture and neutralize with approximately 1.0 *N* H_2SO_4 until the lower layer is distinctly pink (about 0.2 ml. in excess). Highly sulfated oils at this stage may form three layers instead of two. In such cases, use a fat solvent consisting of a mixture of two parts of ether and one of alcohol. Allow the mixture in the separatory funnel to settle for at least 5 min., draw off the lower layer into another separatory funnel and wash the ether layer with 25 ml. portions of NaCl solution until practically neutral to methyl orange, that is, until 1 drop of 0.5 *N* NaOH turns the wash water strongly alkaline. Allow all separations to settle for at least 5 min. Combine the water layers and extract with two 25 ml. portions of ether. Combine the last two ether extractions and wash with NaCl solution until free from acid, as in the case of the ether layer in the first funnel. Combine all the ether layers in the decomposition flask and evaporate the ether.

4.3 *Increase in Acidity upon Boiling, F.* Determine the increase in acidity upon boiling in accordance with the procedure described for Method H42, par. 4.3. Reserve the titrated solution for the subsequent determination of total desulfated fatty matter (Method H45). Make a blank determination as described for Method H42, par. 4.3.2. Calculate the increase in acidity F in accordance with Method H42, par. 4.3.2.

5. RESULTS

5.1 Calculate the percentage of organically combined sulfuric anhydride as follows:

Organically combined sulfuric anhydride (extraction-titration test) per cent $= 0.1426 \times F$

where:

0.1426 = one-tenth the molecular ratio of SO_3:KOH, and
F = the increase in acidity upon boiling.

6. HISTORY

6.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45) of the

American Society for Testing Materials, and is published with their permission.

A.L.C.A. Provisional Method, March 1954

ORGANICALLY COMBINED SULFURIC ANHYDRIDE (H44)

ASH-GRAVIMETRIC TEST (IN THE PRESENCE OF TRUE SULFONATES)

1. SCOPE

1.1 This method of analysis determines the organically combined sulfuric anhydride existing in a sample of sulfonated or sulfated oil, or both, by extracting the undecomposed sulfonated or sulfated fat and other fatty matter over an acidulated, concentrated salt solution, and ashing the purified extract. This method is applicable to all types of sulfonated and sulfated oils, including true sulfonic acid oils and those containing sodium acetate or similar partially titrated compounds.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J10.

3. REAGENTS

3.1 Ethyl Ether, U.S.P.

3.2 Sodium Chloride. Solid, c. p. NaCl.

3.3 Sodium Sulfate. Anhydrous, c. p. Na_2SO_4.

3.4 Methyl Orange (0.1 per cent). Prepare a 0.1 per cent water solution of methyl orange indicator.

4. PROCEDURE

4.1 The procedure consists of isolating and purifying the fatty matter as it exists in the original oil by dissolving the sample in a solvent, acidifying and washing with saturated brine, and ashing the purified extract. If the sample contains ammonia, the ammonia shall first be expelled before the determination is made on the sample.

4.2 *In the Absence of Ammonia.* Proceed as described in the separation of purified oil (Method H43, par. 4.2), combining the ether layers in the first funnel rather than in the decomposition flask. Carefully remove any water that may settle and dehydrate the ether layer as follows: add 5 g. of anhydrous Na_2SO_4, shake vigorously for 5 min. and filter directly into a 150 ml. beaker, placed in a bath of warm water. Wash the flask and filter with ether until free from fat (absence of oil stains on the filter paper after drying) and add the filtrate to the beaker. To avoid creeping of the oil, the volume in the beaker should at no time during the filtering and washing exceed 50 ml. (one-third full).

4.3 Evaporate the ether solution until the volume has been reduced to about 20 ml. and transfer the residue to a tared 50 ml. crucible (high form). Immerse the crucible in a 100 ml. beaker containing warm water until practically all of the ether has evaporated. Rinse the beaker with two 10 ml. and three 5 ml. portions of ether, or until all of the oil has been transferred to the crucible; allow each portion of rinsing ether to evaporate before the next rinsing is made. Burn gently the solvent-free residue and finally ignite at a dull red heat to constant weight.

4.4 To prevent creeping of the oil and to hasten evaporation, stir the solution with a glass rod; before the oil is burned, wipe the rod clean with ashless filter paper and add the paper to the crucible. To oxidize traces of carbon or sodium sulfide that might form, moisten the ash with hydrogen peroxide (30 per cent) and again carefully ignite to constant weight. Calculate the percentage of ash as follows:

$$\text{Extracted ash, per cent} = \frac{\text{Wt. of ash in grams}}{\text{Wt. of sample in grams}} \times 100$$

4.5 *In the Presence of Ammonia.* Dissolve 5 to 8 g. of the sample in 80 ml. of water in a 300 ml. beaker. Add 10 ml. of 1.0 *N* NaOH and boil the solution gently until wet litmus paper no longer indicates ammonia. Cool the solution, transfer to a 300 ml. separatory funnel and add about 35 g. of solid NaCl or enough to make the final solution a 25 per cent NaCl solution. Add 5 drops of methyl orange and complete the neutralization, extraction, etc., in accordance with the procedure described in par. 4.2.

5. RESULTS

5.1 Calculate the percentage of organically combined sulfuric anhydride as follows:

$$\text{Organically combined sulfuric anhydride per cent} = 1.1267 \times \text{extracted ash, per cent}$$

where:

1.1267 = the molecular ratio of $2SO_3$:Na_2SO_4.

6. HISTORY

6.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M., Designation: D 500-45) of the American Society for Testing Materials and is published with their permission.

A.L.C.A. Provisional Method, March 1954

TOTAL DESULFATED FATTY MATTER (H45)

(For Sulfated Oils)

1. SCOPE

1.1 This method of analysis determines the total desulfated fatty matter in a sample of sulfated oil by decomposition with diluted mineral acids and extraction of the decomposed fat. This method is not applicable to samples that are not completely decomposed upon boiling with mineral acids.

2. SPECIMEN

2.1 The sample is obtained from Method H42, par. 4.3.1 or Method H43, par. 4.3.

3. REAGENTS

3.1 Sulfuric Acid (Approximately 1.0 *N*).

3.2 Ethyl Ether, U.S.P.

4. PROCEDURE

4.1 The procedure consists in decomposing the sample with sulfuric acid, extracting the fatty matter with ether, evaporating the solvent, and weighing the residue. After cooling, transfer the titrated solution obtained after determining organically combined sulfuric anhydride in accordance with Method H42, par. 4.3.1. or Method H43, par. 4.3 into a 250 ml. separatory funnel and shake with 50 ml. of ether. Draw off the water layer into another separatory funnel and extract twice with 25 ml. portions of ether. Wash the combined ether layers with 15 ml. portions of saturated salt water until the wash water is neutral to methyl orange. Transfer the ether layer to a 150 ml. beaker and evaporate to dryness. The dried mass is then dissolved in 50 ml. of a mix containing 50 per cent alcohol and 50 per cent water and transferred to a separatory funnel. Rinse beaker with a like 50 per cent alcohol, mix into funnel and extract this with an ether mixture consisting of 3 parts of petroleum ether and 1 part of ethyl ether, using three consecutive portions of the ether mix. Reject the alcohol water portion which contains the undecomposed sulfonates.

4.2 Transfer combined ether extractions to a tared 125 ml. assay flask. Dry to constant weight and record weight. This dried mass contains total desulfated fatty matter plus unsaponifiables. Proceed with the determination for unsaponifiables as described in Method H47. The difference between the total weight recorded above and the unsaponifiable matter will be the correct weight for Total Desulfated Fatty Matter.

5. RESULTS

5.1 Calculate the total desulfated fatty matter as follows:

$$\text{Total desulfated fatty matter, per cent} = \frac{\text{wt. of residue in grams}}{\text{wt. of sample in grams}} \times 100$$

6. HISTORY

6.1 This method is a modified part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45) of the American Society for Testing Materials and is published with their permission.

A.L.C.A. Provisional Method, March 1954

TOTAL ACTIVE INGREDIENTS (H46)

1. SCOPE

1.1 This method of analysis determines the total active ingredients in a sample of sulfonated or sulfated oil, or both, as it exists in the original sample by extracting the undecomposed sulfonated or sulfated fat and other fatty matter over an acidified concentrated salt solution. Free alkali or alkali bound as soap is not included.

1.2 In the case of sulfated oils only, this determination may also be estimated by calculation as it is equivalent to the sum of the desulfated fatty matter and neutralized organically combined sulfuric anhydride.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

3. REAGENTS

3.1 Ethyl Ether, U.S.P.

3.2 Sodium Chloride. Solid, c. p. NaCl.

3.3 Sodium Sulfate. Anhydrous, c. p. Na_2SO_4.

3.4 Methyl Orange (0.1 per cent). Prepare a 0.1 per cent water solution of methyl orange indicator.

3.5 Alcoholic Potassium Hydroxide (0.5 *N*). Accurately standardize a 0.5 *N* alcoholic KOH solution the strength of which shall be expressed as milligrams of KOH per milliliter; 1 ml. of 0.5 *N* alcoholic KOH is equivalent to 28.05 mg. of KOH.

4. PROCEDURE

4.1 The procedure consists of isolating and purifying the fatty matter as it exists in the original oil by dissolving the sample in a solvent, acidifying and washing with saturated brine, and weighing the purified extract. Proceed

as described in the determination of organically combined sulfuric anhydride, Method H44, in the absence of ammonia (par. 4.2), retaining the separated active ingredients in the 150 ml. beaker instead of transferring it to a crucible. Evaporate the filtrate to a total volume of about 20 ml., add exactly 2 ml. of alcoholic KOH, mix the contents by swirling, and finally evaporate until practically free from ether.

4.1.1 With highly sulfonated or sulfated oil, it may be necessary to add 5 to 10 ml. of the alcoholic KOH in order to stabilize the residue.

4.2 Dry the residue at 108° to 112°C. for 1.5 hr., cool in a desiccator and weigh. Repeat the heating for 30 min. periods until constant weight is obtained.

5. RESULTS

5.1 *Correction for the Alkali Added.* Calculate the correction for the alkali added as follows:

$$\text{Correction for alkali added, grams} = 0.000679 \text{ (ml. of KOH x S)}$$

where:

0.000679 = molecular ratio of (K – H):KOH divided by 1000, and
S = strength of the KOH in milligrams of KOH per milliliter.

5.2 *Total Active Ingredients.* Calculate the total active ingredients as folows:

$$\text{Total active ingredients, per cent} = \frac{\text{grams residue - alkali correction}}{\text{wt. of sample in grams}} \times 100$$

5.3 *Total Active Ingredients Calculation Method (For Sulfated Oils Only).* Calculate the total active ingredients by the calculation method which is applicable to sulfated oils only, as follows:

$$T = P + \frac{NaSO_4^- \times Y}{SO_3}$$

or

$$T = P + 1.4875 \times Y$$

where:

T = total active ingredients in per cent,
P = total desulfated fatty matter in per cent, and
Y = percentage of combined SO_3.

5.3.1 The factor 1.4875 is based on the assumption that the desulfated fatty matter becomes polymerized at the point where the SO_3 splits off and no hydroxyl groups are formed. If the latter are formed the factor becomes $\frac{NaSO_4^- - 1}{SO_3} = 1.275$. Calculated results were in better aggreement with actual determinations when the higher factor was used.

6. HISTORY

6.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45) of the American Society for Testing Materials, and is published with their permission.

A.L.C.A. Provisional Method, March 1954

UNSAPONIFIABLE NONVOLATILE MATTER (H47)

(For Sulfated Oils)

1. SCOPE

1.1 This method of analysis determines the unsaponifiable, nonvolatile (above 80°C.) matter existing in a sample of sulfated oil by saponifying the desulfated fatty matter and extracting the unsaponifiable matter and extracting the unsaponifiable matter from the soap solution with ethyl ether.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

3. APPARATUS AND REAGENTS

3.1 Saponification Flask. The apparatus required for the saponification consists of a glass flask provided with an air condenser and identical with the apparatus described in Method H42 for organically combined sulfuric anhydride (pars. 3.1.1 and 3.1.2).

3.2 Potassium Hydroxide Solution (0.5 *N.*). Prepare an approximately 0.5 *N* aqueous KOH solution.

3.3 Alcoholic Potassium Hydroxide (0.5 *N.*). Prepare an approximately but not less than, 0.5 *N* alcoholic KOH solution.

3.4 Ethyl Ether, U.S.P.

4. PROCEDURE

4.1 The procedure consists in decomposing the sample with mineral acid, extracting the desulfated fatty matter, saponifying the latter, and extracting the unsaponifiable matter from the soap solution with ethyl ether.

4.2 *Desulfated Fatty Matter.* Determine the desulfated fatty matter as described in the determination of total desulfated fatty matter (Method H45).

4.3 *Saponification.* Accurately weigh 2 to 2.5 g. of the desulfated fatty matter in the flask, add 25 ml. of the alcoholic KOH, and simmer the contents (without loss of alcohol) for 1 hr. with occasional swirling, over an electric hot plate or other source of heat.

4.4 *Extraction.* Transfer the contents of the flask to a 250 ml. separatory funnel and wash the flask several times with a total of 50 ml. of water, pouring it into the separatory funnel. Extract the solution while still warm (about 30°C.) with 50 ml. of ether (rinse the saponification flask with the ether before adding it to the separatory funnel), shaking vigorously for about 1 min., and allow the layers to settle and clear. Draw off the lower layer in a second 250 ml. separatory funnel and extract in a similar manner with two 50 ml. portions of ether.

4.5 *Preliminary Water Washing.* Add 20 ml. of water to the combined ether layer, turn the separatory funnel and contents over gently about six times and allow the layers to settle and clear. Draw off the lower layer and discard. Wash the ether layer twice more with 20 ml. portions of water, shaking vigorously after each addition.

4.6 *Alkali and Water Washing.* Add 20 ml. of 0.5 *N* KOH to the washed ether layer, turn the separatory funnel and contents over gently about six times, and allow the layers to settle and clear. Draw off the lower layer and discard. Wash the ether layer with 20 ml. of water, shaking vigorously. Continue washing with 20 ml. of 0.5 *N* KOH followed by 20 ml. of water, shaking vigorously after each addition, until the alkali layer upon strong acidification with HCl and settling for a few minutes is only faintly opalescent. Finally wash the ether layer with 20 ml. portions of water until the wash water is no longer pink to phenolphthalein.

4.7 *Solvent Removal.* Transfer the ether layer to a 150 ml. beaker (counterbalance the beaker if the amount of unsaponifiable matter is small and important) and evaporate over a hot-water bath until practically free of ether. Heat the beaker at 75° to 80°C. until constant weight is obtained.

4.8 A 30 per cent alcoholic solution by volume is the most satisfactory solution from which to extract the unsaponifiable matter.

4.8.1 If emulsions form, add 5 ml. of alcohol, pouring it down the side of the funnel.

4.8.2 It is important to maintain the volume of ether at not less than 150 ml., otherwise small quantities of unsaponifiable matter may be lost.

4.8.3 To check whether or not the unsaponifiable matter is free from fatty acids, dissolve the residue in 10 ml. of freshly boiled neutral alcohol and titrate with 0.1 *N* alcoholic KOH solution, using phenolphthalein as the indicator. Not more than 0.1 ml. should be required for neutralization. If more is required, the determination has not been carried out effectively and must be repeated.

5. RESULTS

5.1 Calculate the unsaponifiable matter as follows:

$$U = \frac{R}{G} \times P$$

where:

U = unsaponifiable nonvolatile matter, per cent,
R = weight of residue in grams,
G = weight of desulfated fatty matter in grams, and
P = percentage of desulfated fatty matter.

6. HISTORY

6.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45) of the American Society for Testing Materials, and is published with their permission.

A.L.C.A. Provisional Method, March 1954

INORGANIC SALTS (H48)

1. SCOPE

1.1 This method of analysis determines in a sample of sulfonated or sulfated oil, or both, the inorganic sulfates, chlorides, and all other salts that are insoluble in a mixture of oleic acid and carbon tetrachloride.

2. SPECIMEN

2.1 The sample shall be taken as described in Method J50.

3. APPARATUS AND REAGENTS

3.1 Either a Gooch crucible or filter paper may be used for filtering. Ignite the Gooch crucible in a larger crucible, supported by an asbestos ring and assembled as shown in Figure H48. If filter paper is used, it may be a 9 cm. Whatman No. 40 or similar grade of ashless filter paper.

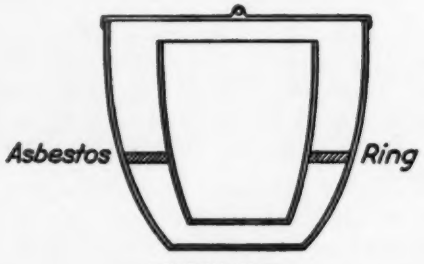


FIGURE H-48

3.2 Oleic Acid, U.S.P.

3.3 Carbon Tetrachloride, U.S.P.

3.4 Ethyl Ether, U.S.P.

3.5 Asbestos. Asbestos fiber, alkali and acid washed.

4. PROCEDURE

4.1 The procedure consists of dehydrating the sample, dissolving in a solvent, filtering, igniting, and weighing the residue. In the presence of ammonium salts, the residue is not ignited but only dried to constant weight. The presence of sodium acetate does not interfere with this method.

4.2 *In the Absence of Ammonium Salts.* Weigh 3 to 5 g. of the sample and place in a 250 ml. beaker, add an approximately equal amount of oleic acid, and heat the mixture on an oil bath, while stirring constantly with a thermometer, at a temperature of 105° to 110°C. until practically free from water. Continue the heating until the temperature of the contents reaches 118° to 120°C. and maintain at that temperature for about 5 min. If the dehydrated sample upon cooling does not remain liquid, add more oleic acid. Dissolve the dehydrated sample in 100 ml. of CCl_4 warmed to 50° to 55°C. and filter through a counterpoised filter paper or a Gooch crucible.

4.3 Prepare the Gooch crucible by passing a thin emulsion of asbestos fiber in water through the crucible until a pad of about 2 mm. in thickness is formed. Dry the asbestos pad and ignite for 30 min. at first gently and finally more strongly. Then pass 75 ml. of CCl_4 through the crucible and again ignite the asbestos pad, cool in a desiccator, and weigh. Repeat the process of washing with CCl_4 until there is no further loss in weight.

4.4 Wash the residue with three 15 ml. portions of a solution of oleic acid in CCl_4 (2 per cent), then with six 15 ml. portions of hot CCl_4, and finally with two 15 ml. portions of ether or until the residue is free from oil. Take care that the top of the filter is thoroughly washed. Transfer the last traces of the residue to the filter by allowing the solvent to evaporate when the salts become free flowing. Dry the residue at 125° to 130°C. for 45 min., cool in a desiccator and weigh. Ignite the residue at a dull red heat for 15 min., weigh, and repeat the ignition until constant weight is obtained.

4.5 *In the Presence of Ammonium Salts.* Proceed as described in par. 4.2 for the determination of inorganic salts in the absence of ammonium salts with the following exceptions: (1) in preparing the Gooch crucible, do not ignite but heat it at 125° to 130°C. for 45 min. and repeat the heating until constant weight is obtained, and (2) heat the residue, whether in a Gooch crucible or on a filter paper as in (1) but do not ignite it.

5. RESULTS

5.1 The method of calculation depends upon whether or not ammonium salts are present in the sample.

5.2 Calculate the inorganic sulfates and chlorides including ammonium salts as follows:

Inorganic sulfates and chlorides, including ammonium salts, per cent =

$$\frac{\text{wt. of dried residue in grams}}{\text{wt. of sample in grams}} \times 100$$

5.3 Calculate the nonvolatile inorganic sulfates and chlorides (in the absence of ammonium salts) as follows:

Nonvolatile, inorganic sulfates and chlorides, per cent =

$$\frac{\text{wt. of ignited residue in grams}}{\text{wt. of sample in grams}} \times 100$$

5.3.1 In the absence of ammonium salts, the difference between the percentage of the dried residue and the percentage of the ignited residue shall not be greater than 0.25 per cent.

6. HISTORY

6.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45) of the American Society for Testing Materials, and is published with their permission.

A.L.C.A. Provisional Method, March 1954

TOTAL ALKALINITY AND TOTAL AMMONIA (H49)

1. SCOPE

1.1 *Total Alkalinity.* This method of analysis determines the total alkalinity existing in a sample of sulfonated or sulfated oil, or both, by titrating a water solution of the sample with mineral acid in the presence of methyl orange as the indicator. This method determines the total alkalinity of the fixed alkali, ammonia and triethanolamine bound as soap, free alkali, and the alkalinity of titratable alkaline salts, but not that of non-titratable alkaline salts.

1.2 *Total Ammonia.* This method of analysis determines the total ammonia in a sample of sulfonated or sulfated oil, or both, by boiling a water solution of the sample with excess alkali and determining by titration the loss in alkali after the boiling.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

3. PROCEDURE

3.1 The procedure consists of two determinations: namely, (*a*) the total alkalinity, and (b), the loss in alkalinity after boiling with excess NaOH.

3.2 *Total Alkalinity.* Determine the total alkalinity as described in the determination of organically combined sulfuric anhydride, Method H42, par. 4.2.

3.3 *Alkalinity After Boiling.* Dissolve 10 g. of the sample in 100 ml. of water in a 500 ml. beaker, add 25 ml. of 0.5 *N* NaOH, and boil the mixture for 30 min. or until all the ammonia is expelled as indicated by moistened red litmus paper. Cool the contents of the beaker, add methyl orange indicator (0.1 per cent) and titrate to an approximate end point. Transfer the mixture to a 250 ml. glass-stoppered flask and complete the titration (with the addition of salt and ether) as described in the determination of organically combined sulfuric anhydride, Method H42, par. 4.3.

4. RESULTS

4.1 Calculate the total alkalinity, A, as follows:

$$A = \frac{(B \times D) - (C \times E)}{W}$$

where:

A = total alkalinity in milligrams of KOH per gram
B = milliliters of acid
C = milliliters of alkali
D = strength of the acid in milligrams of KOH per milliliter
E = strength of the alkali in milligrams of KOH per milliliter
W = weight of sample in grams

4.2 Calculate the total ammonia as follows:

$$T = A + \frac{(B \times D) - (C \times E)}{W}$$

or

$$\text{Total ammonia, per cent} = 0.0303\ T$$

where:

T = total ammonia in milligrams of KOH per gram,
A = total alkalinity in milligrams of KOH per gram,
B = milliliters of alkali added,
C = milliliters of acid added,
D = strength of the alkali as milligrams of KOH per millilieter,
E = strength of the acid as milligrams of KOH per milliliter, and
W = weight of the sample in grams.

5. HISTORY

5.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45)

of the American Society for Testing Materials, and is published with their permission.

A.L.C.A. Provisional Method, March 1954

ACIDITY AS FREE FATTY ACIDS OR ACID NUMBER (H50)

IN THE ABSENCE OF AMMONIUM OR TRIETHANOLAMINE SOAPS

1. SCOPE

1.1 This method of analysis determines the acidity as free fatty acids existing in a sample of sulfonated or sulfated oil, or both, by titrating the sample dissolved in a solvent. It is not applicable in the presence of ammonium or triethanolamine soaps or salts, or other compounds which do not react neutral to phenolphthalein when dissolved in alcohol.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

3. PROCEDURE

3.1 The procedure consists of titrating a solution of the sample in a mixture of alcohol and ether in the presence of phenolphthalein indicator. Dissolve 10 g. of the sample in a mixture of 50 ml. of neutral alcohol and 25 ml. of ether, add five drops of phenolphthalein indicator, and titrate the solution with 0.5 *N* NaOH or KOH until the pink color persists after vigorous shaking.

4. RESULTS

4.1 Calculate the acidity as free fatty acids, as follows:

$$K = \frac{C \times E}{W}$$

where:

K = acidity as free fatty acids or acid number, in milliliters of KOH per gram,
C = milliliters of alkali,
E = strength of the alkali as milligrams of KOH, and
W = weight of sample in grams.

5. HISTORY

5.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45) of the American Society for Testing Materials, and is published with their permission.

A.L.C.A. Provisional Method, March 1954

ACIDITY AS FREE FATTY ACIDS OR ACID NUMBER (H51)

IN THE PRESENCE OF DARK COLORED OILS BUT IN THE ABSENCE OF AMMONIUM OR TRIETHANOLAMINE SOAPS (BRINE METHOD)

1. SCOPE

1.1 This method of analysis determines the acidity as free fatty acids existing in a sample of sulfonated or sulfated oil, or both, by titrating a water solution of the sample with phenolphthalein as the indicator. It is not applicable in the presence of ammonia or triethanolamine soaps or acid salts.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

3. PROCEDURE

3.1 The procedure consists in titrating a water solution of the sample in the presence of salt, ether and alcohol with phenolphthalein as the indicator. Dissolve 10 g. of the sample in 100 ml. of water contained in a 250 ml., glass-stoppered, Erlenmeyer flask, warming to obtain solution, if necessary. After cooling, add 30 g. of NaCl, 25 ml. of ether and 50 ml. of neutral alcohol.

3.1.1 At this stage, methyl orange indicator may be added and the total alkalinity determined as described in the determination of organically combined sulfuric anhydride, Method H42, par. 4.2.

3.2 Add five drops of phenolphthalein indicator (1.0 per cent alcoholic solution) and titrate the contents of the flask with 0.5 *N* NaOH until the first pink tinge appears in the water layer, shaking vigorously after each addition of the reagent.

4. RESULTS

4.1 Calculate the acidity as free fatty acids as described in the determination of acidity as free fatty acids, Method H50, par. 4.1.

4.1.1 In case the total alkalinity was determined on the same sample the acidity of the free fatty acids is calculated as follows:

$$K = \frac{C \times E}{W} - A$$

where:

K = acidity as free fatty acids or acid number, in milligrams of KOH per gram,
C = milliliters of alkali,
E = strength of the alkali as milligrams of KOH,
A = total alkalinity, and
W = weight of sample in grams.

5. HISTORY

5.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45) of the American Society for Testing Materials, and is published with their permission.

A.L.C.A. Provisional Method, March 1954

ACIDITY AS FREE FATTY ACIDS OR ACID NUMBER (H52)

In the Presence of Ammonium or Triethanolamine Soaps

1. SCOPE

1.1 This method of analysis determines the acidity as free fatty acids in the presence of ammonium or triethanolamine soaps, or both, existing in a sample of sulfonated or sulfated oil, or both, by calculation from the total alkalinity and the free-and-alkali-combined fatty acids.

2. SPECIMEN

2.1 The sample shall be taken in accordance with Method J50.

3. PROCEDURE

3.1 The procedure consists of two determinations: namely, (*a*) total alkalinity, and (*b*) free-and-alkali-combined fatty acids.

3.2 *Total Alkalinity.* Determine the total alkalinity as described in the determination of organically combined sulfuric anhydride, Method H42, par. 4.2.

3.3 *Free-and-Alkali-Combined Fatty Acids.* Extract the total sulfated and sulfonated fatty matter as described in the determination of total active ingredients (Method H46, par. 4.), but omit the dehydration of the extract.

3.3.1 In the presence of acetates, wash the ether layer carefully with concentrated NaCl solution until one or two drops of 0.5 *N* NaOH added to the final wash water are neutral to phenolphthalein indicator.

Add exactly 0.5 ml. of 0.5 *N* NaOH to the extract, evaporate the ether to a volume of about 25 ml. add approximately 50 ml. of neutral alcohol, and titrate the mixture with 0.5 *N* NaOH to a phenolphthalein end point.

4. RESULTS

4.1 Calculate the free-and-alkali-combined fatty acids as described in the determination of acidity as free fatty acids, Method H50, par. 4.1. Calculate the acidity as free fatty acids in the presence of ammonium or triethanolamine soaps, or both, as follows:

$$K = J - A$$

where:

K = acidity as free fatty acids or acid number in milligrams of KOH per gram,

J = free-and-alkali-combined fatty acids, and

A = total alkalinity.

5. HISTORY

5.1 This method is part of the Standard Methods of Chemical Analysis of Sulfonated and Sulfated Oils (A.S.T.M. Designation: D 500-45) of the American Society for Testing Materials, and is published with their permission.

A.L.C.A. Provisional Method, March 1954

NEUTRAL FATTY MATTER (H53)

1. SCOPE

1.1 The method for Neutral Fatty Matter should include all degraded glycerides, since they are neutral fats. However, this procedure does not necessarily determine all the mono and diglycerides that may be present in the sample. This is due to the water soluble characteristics of some mono and diglycerides.

2. SPECIMEN

2.1 The sample shall be taken as described in Method J50.

3. PROCEDURE

3.1 Weigh 5 g. of sample into a 125 ml. assay flask and add 50 ml. of alcohol. Warm and rotate, if necessary, to dissolve. Titrate with 0.5 *N* NaOH to end point using phenolphthalein indicator. Cool, then add 1 ml. excess 0.5 *N* NaOH and rotate flask. Extract three times with 50 ml. portions of petroleum ether and wash combined ether layers with water until free from alkali. Evaporate ether and dry to constant weight.

4. RESULTS

4.1 The total neutral oily matter is calculated as follows:

$$\text{Total neutral oily matter} = \frac{\text{weight of residue} \times 100}{\text{weight of sample}}$$

4.2 The total neutral oily matter includes unsaponifiables, if any, which should be determined as in Method H47 and subtracted, to obtain Neutral Fatty Matter.

A.L.C.A. Provisional Method, March 1954

A Study of the Mechanism of Leather Dyeing**

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Although dyeing is one of the more important processes in converting tanned skins into a saleable product, there has been relatively little experimental work attempted to elucidate the exact nature of the mechanism by which this is accomplished. Only in the past few years, in the work of a very few investigators, has any attempt to define the nature of the forces involved been made. Yet, in this same period, great strides have been made on this same problem in connection with other proteins and polyamide materials which, fundamentally, are very similar to collagen, the basic protein of skin and hide. With this background of work on similar proteins and the more recent investigations of leather, this study was initiated in an attempt to more fully investigate the details of the dyeing mechanism.

This paper has confined its scope to chrome tanned leathers dyed with anionic dyes of the simple monazo type. This restriction still includes one of the principle tannages and one of the more important classes of dyes.

Historical

The earliest investigations of leather dyeing were primarily concerned with demonstrating a stoichiometric combination of the dye with the leather, and the formation of salt linkages was either recognized or inferred [3, 4, 5, 15, 20, 21, 34, 46]. A rather similar view, but also postulating a mechanism requiring a Donnan semi-permeable membrane, was taken by Elod and Kohnlein [14]. However, Vickerstaff points out that this theory does not satisfactorily account for the differences in the affinities of similar dyes in the case of wool [52], and the same argument must necessarily hold with leather. Nevertheless, work on other proteins has indicated that electrostatic forces may not be ignored.

The role of secondary binding forces between the dye and collagen has not received much attention, although Gustavson [18] suggested their importance in 1926. Cockbain has also speculated that hydrogen bonding must be a major factor [8], although he has offered no experimental evidence in this regard. More recently Otto [38] has shown that the pi, or mobile, electrons of conjugated double bond systems play a definite role in binding dyes to leather, leading to secondary forces which reinforce electrostatic bonds.

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Studies on proteins other than collagen have given much more evidence of the importance of these secondary bonding forces (i. e. hydrogen bonds and van de Waal forces) [1, 11, 12, 22, 40, 41, 43, 44, 45]. Klotz and his coworkers [25, 26, 27, 28, 29, 30] especially have amassed a large amount of evidence showing that these weak forces explain the differences in the binding of dyes of similar structure. They have shown that dyes with the same number of polar groups, but differing in the size of their aromatic rings, have increased binding affinity for the protein with increased molecular weight, and conclude that these differences are due to van der Waal interactions. Teresi and Luck [48] have shown that increasing the length of side chains of aromatic carboxylic acids also increases the binding energy and this increase is probably due to the effect of additional residual valency forces. Gilbert [17] has also shown that replacement of the benzene ring of several dyes by a naphthalene ring increases the affinity of the dyes for wool, and concludes that secondary forces must be important.

Karush [22, 23, 24] and Cogin and Davis [9] indicate that there are also differences in the reactivity of the sites on the protein and that configurational differences of both the dye and the protein contribute toward differences in the binding. These conclusions are based on studies of competition between dyes and detergents for the protein sites at various concentrations. Teresi [47] has also shown, by modifying the ϵ-amino groups of lysine and the guanidinal groups of arginine with formaldehyde, that methyl orange does not bind at the same sites as nitrophenolates. And with wool, Speakman, and Elliott [42] indicate that deamination reduces dye affinity, but that combination with weak acids is not solely through the amino group.

There is additional evidence from the investigations of nylon, a polyamide free from the confusing effects of varying side chains, that both electrostatic and hydrogen bonding to the peptide groups occur [7, 33, 52]. This is shown by the ability of nylon to bind amounts of dye far in excess of that accounted for by the free amino groups. However, Klotz [25] has demonstrated that dyes with phenolic groups para to the azo linkage are bound more readily than those with the phenolic group in the ortho position. He attributes this difference to the ability of the latter to form an intramolecular hydrogen bond and the stronger interaction of the para isomer with the solvent.

In the specific case of chrome tanned collagen, consideration must also be given to the possibility of reaction of the dye with the chrome complex. Elod and Hansel [13] stated that, in the dyeing of chrome leather, part of the dye is combined with the protein and part of the dye with the complex. Otto [37] has recently shown that anionic dyes will penetrate the basic chrome complexes in solution, and states that this also occurs on the leather, with the degree of such combination being determined by the ratio of the molecular weight to the number of sulfonic acid groups on the dye. Tewari and Ohosh [49] and Bailar and Callis [2] have also shown that both acid and basic dyes can be bound by hydrated chromic oxide.

Therefore, this study of the dye-leather system considered four types of bonding forces to have some influence in the dye-chrome leather reaction: (1) electrostatic bonds or salt links, between the free amino groups of the protein and the sulfonic acid groups of the dyes. (2) hydrogen bonds between the active hydrogens of the dye and the centers of high electron density on the protein, or between the active hydrogens of the leather and the azo linkage of the dye. (3) short range van der Waal, or residual valency, forces between the dye and the protein, and (4) coordinate-covalent bonds between the dye and the chrome complex. From other investigations these types of forces have been shown to occur in dye-protein or dye-chrome systems. Strict covalent bonding has not been seriously considered for these systems in the past, and has not been investigated in this work.

Experimental

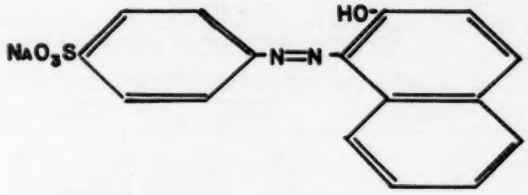
Considering the relatively small amount of information on the mechanism of leather dyeing mentioned above, a study of the forces involved in the dye-leather reaction was made following two different approaches. The classical investigation of the dyeing rate (or rate of dyebath exhaustion), used successfully to determine the factors affecting the take up of dye on wool and other fibers, was investigated, and then a study was made of the ease of removal of the dye from the dyed leather with agents that are known to break specific types of bonds. The results of these approaches were then used to explain how the dye is taken up by the leather from the bath and the forces involved in holding the dye to the leather.

Dyeing Rate Pickled calfskin squares were randomly selected from the bend area and grouped for tannage. Four different tannages were then done, the conditions being such that each type of resulting leather contained the same amount of chrome (about 4.7 per cent as the oxide on the dry weight basis). One group was tanned with an unmasked sulfur dioxide reduced chrome liquor, another with formate masked SO_2 reduced liquor, the third with tartrate masked SO_2 reduced liquor, and the final group was tanned with an unmasked SO_2 reduced chrome liquor and then retanned with formaldehyde (one per cent on the wet, pickled weight). The liquors were all 31 per cent basic and free of components other than the chrome salt and masking agent. The tanned samples were all neutralized to pH 3.5 and then dyed.

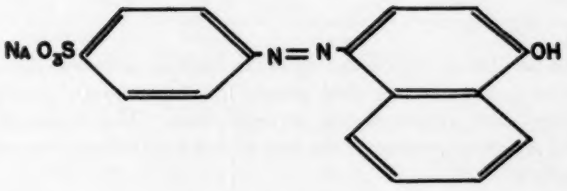
All samples were conditioned for dyeing by placing them in 1000 per cent acetate buffer for 16 hours at pH 3.6 or 4.7 according to the experimental plan. The pieces were then removed and placed in one quart jars containing 0.0001 moles of the appropriate dye (Table I) per gram of wet, tanned leather with enough water to give a float with a ratio of 3:1 and having a final buffer concentration of 0.2 *N* acetate buffer at the correct pH. The dveing was carried out in the launderometer at 120°F. Samples of the dye

TABLE I
FORMULAE OF DYES USED

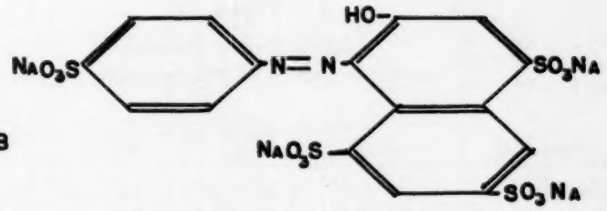
ORANGE II
C. I. 151



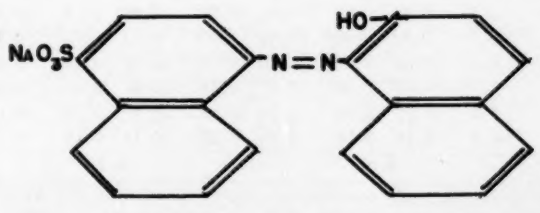
ORANGE I
C. I. 150



RED II
SYNTHESIS
IN THIS LAB



FAST RED A
C. I. 176



bath were examined at various time intervals and the dye bath concentrations at these times determined spectrophotometrically. At the end of four hours, the rate of exhaustion was fairly constant and the samples were removed and washed with 500 per cent water. The leathers were then pressed at 4000 pounds per square inch to remove any excess free liquor and allowed to dry. The amount of dye remaining in the combined exhaust liquor and washing was determined (that removed by pressing was negligible) and the difference

between this and the amount fed was calculated as the amount of dye bound by the leather (Table II).

TABLE II

Dye Bound

Expressed as moles x 10^4 per gram dry leather

Dye	Tannages							
	Unmasked		Formate Masked		Tartrate Masked		Formaldehyde Treated	
Orange II	2.63	2.75	2.59	2.89	2.61	2.89	2.40	2.50
OrangeI	2.67	2.61	2.51	2.52	2.52	2.47	2.24	2.28
Fast Red A	2.33	2.19	2.24	2.17	2.05	2.27	2.02	1.95
Red II	1.62	1.57	1.60	1.53	1.49	1.48	1.42	1.24

The amount of dye remaining in the bath at each time interval was plotted and the curves were rectified, graphs for the reciprocal of the dye remaining vs. time gave approximately straight lines. The slopes of these rectified curves are an expression of the rate of dye bath exhaustion and are tabulated in Table III.

TABLE III

Rate of Dyebath Exhaustion

Expressed in Units of 10^5/reciprocal moles per hour

Dye and pH		Tannages								
		Unmasked		Formate Masked		Tartrate Masked		Formaldehyde Treated		Means
Orange II	3.6	1.27	1.09	1.33	1.12	1.14	1.04	0.88	0.94	1.10
	4.7	1.02	0.96	1.18	0.92	0.71	0.72	0.55	0.53	0.82
Orange I	3.6	0.83	0.97	0.93	1.09	0.98	0.75	0.79	0.64	0.87
	4.7	0.82	0.80	0.89	0.90	0.73	0.72	0.53	0.49	0.74
Fast Red A	3.6	0.61	0.61	0.80	0.67	0.52	0.54	0.50	0.48	0.59
	4.7	0.45	0.48	0.47	0.44	0.42	0.47	0.36	0.36	0.43
Red II	3.6	0.21	0.22	0.20	0.21	0.21	0.22	0.13	0.15	0.19
	4.7	0.18	0.18	0.18	0.16	0.14	0.16	0.10	0.08	0.15
Means		0.67		0.72		0.59		0.47		

Dye Removal Each of the above dyed samples after drying was ground in the Wiley Mill and subdivided into four groups. Samples of 1.500 gram each, for all of the above dyeings done at pH 3.6, were washed with water, five per cent sodium sulfate, one per cent sodium oxalate, or six molar urea. The extraction was carried out in a modified Wilson-Kern apparatus, described by Lollar and Kremen[31], and the wash solutions collected at the rate of one liter per hour. The concentrations of the dye in the wash liquors was

determined spectrophotometrically at various time intervals for five hours. From this data the amounts of dye removed from each sample by each wash solution was calculated (Table IV).

Discussion of Results

Various statistical calculations were made on the data obtained and the following section is based on the results of these analyses. A more complete discussion of the statistics may be found in the Appendix.

TABLE IV

Dye Removed by Washing

Expressed as Moles x 10^4 per gram dry leather

Dyes and Washing Solutions	Tannages								Means
	Unmasked		Formate Masked		Tartrate Masked		Formaldehyde Treated		
Orange II									
Water	0.40	0.38	0.32	0.37	0.61	0.54	0.22	0.23	0.38
Urea	1.18	1.49	1.74	1.26	2.00	1.80	1.54	1.32	1.54
NaOx	2.04	2.05	1.95	2.09	2.01	2.05	1.86	2.06	2.01
Na_2SO_4	1.10	1.04	1.14	1.13	1.25	1.16	0.96	1.16	1.12
Orange I									
Water	0.30	0.40	0.22	0.24	0.34	0.29	0.16	0.17	0.26
Urea	1.63	1.66	1.42	1.43	1.63	1.70	1.14	1.66	1.53
NaOx	2.25	2.12	1.89	1.89	1.89	2.06	1.74	1.67	1.93
Na_2SO_4	1.34	1.58	1.21	1.69	1.11	1.32	1.16	1.48	1.36
Fast Red A									
Water	0.29	0.09	0.25	0.15	0.33	0.37	0.20	0.07	0.22
Urea	1.95	1.48	2.00	1.69	1.59	1.85	1.54	1.87	1.75
NaOx	0.95	0.52	0.69	0.54	0.72	1.06	0.67	1.00	0.77
Na_2SO_4	0.11	0.07	0.05	0.06	0.12	0.10	0.09	0.08	0.08
Red II									
Water	0.18	0.13	0.17	0.09	0.10	0.10	0.10	0.07	0.12
Urea	0.67	0.47	0.65	0.51	0.68	0.58	0.65	0.43	0.58
NaOx	1.09	1.07	1.15	1.05	1.09	1.06	0.91	0.80	1.03
Na_2SO_4	1.07	1.01	1.12	0.97	1.01	0.93	0.77	0.59	0.93
Means	1.00		0.97		1.05		0.89		

The data in Table III indicate a variation between the exhaustion rates of the dyebath for different types of leathers. It will be noted that the means of the unmasked and formate masked leathers are only slightly different, and the statistical "t" test [50] indicates that there is no significant variation between these two tannages in their influence on the exhaustion rate. However, there is a real difference in the mean exhaustion rates of both the tartrate masked and the formaldehyde treated leathers as compared to the unmasked tannage.

Since the means of the formate masked and the unmasked leathers are not significantly different in regard to the ease of dye removal, it is probable that the dye is taken up and deposited on the leather by the same forces in each case, and that there is no difference in the effect of the formate masked tannage and the unmasked tannage with regard to their influence on the dyeing. In other words, the dye seems to displace the formate and the sulfate groups from the chrome complex about equally.

The mean of the tartrate tannage shows a significant departure from that of the unmasked tannage in regards to its effect upon dye bath exhaustion. The former binds less dye, but the dye that is bound, is removed about as easily as the latter (Tables III and IV). Since the only difference in the two leathers is the presence of the tartrate group compared to the sulfate ion, the differences in dyeing rate must be assigned to the tartrate group. The tartrate anion is much more tightly held than the sulfate, and the dye apparently displaces it with difficulty or not at all, thereby limiting the number of sites available to it. Thus the dyeing rate, or the rate of dye bath exhaustion, is reduced, but the dye that is bound, is held as tightly as in the unmasked leather.

Formaldehyde treatment of the chrome tanned leather reduces the number of free amino groups available for the formation of electrostatic bonds with the sulfonic acid groups of the dyes. The significantly lower exhaustion rate of this leather (Table III) may be attributed to the reduction of the number of sites available, or to the decrease in charge on the leather. Careful examination of Table IV indicates that there is slightly more dye removed from the unmasked tannage by sodium sulfate (which acts on electrostatic bonds) than from the formaldehyde treated leather, thus supporting the charge explanation. The charge on the leather is a factor in controlling the rate of exhaustion of the dye, but the dye is bound to the leather chiefly through linkages other than a salt bridge with the free amino groups.

It is apparent from both Tables III and IV that the exhaustion rate and the ease of dye removal are influenced significantly by the constituent groups on the dyes. This is confirmed in the analyses of variance found in the appendix (Tables V and VI). In addition, the rate of exhaustion of the dyebath is influenced by both the pH and the type of tannage for any particular dye, as shown by significant dye-pH and dye-tannage interaction terms. Also, the significant dye-wash and dye-tannage interactions for the dye removal show that these terms are not independent.

It will be noted from Tables III that Orange I exhausts more slowly than Orange II, although these dyes differ only in the position of the phenolic group (See Table I). This difference in rate may be attributed to the stronger interaction of the para phenolic group of Orange I with the solvent, as suggested by Klotz[25]. Then, in the competition between the leather and the solution for the dye, the Orange II is more readily taken up by the leather because of its lower probability of interaction with the solvent than

is Orange I. However, it was also noted that both of these dyes are removed with the same ease from the leather by urea (Table 4). The dyes, having the same hydrogen bonding potential for that amount that has been bound, have different potentials in solution. Then changes in the position of the phenolic groups (between ortho and para) influence the rate of dye bath exhaustion, but do not affect the manner of binding.

The mean exhaustion of Fast Red A was also less than that of Orange II. In this case, the dyes differ in the substitution of a napthalene ring for the benzene ring of Orange II. This leads to an increase in the molecular weight with the consequent increase in the residual, or van der Waal, valency forces, in the Red A molecule, and a shift of the absorption maximum to a higher wave length. To explain the significant decrease in the rate of dye exhaustion, the steric effect of the added ring and the effect of the additional attractive forces to give aggregation may be theorized. The latter undoubtedly play some role and the lower solubility of Fast Red A (compared to Orange II) gives some evidence for this. Since the rate of diffusion of the dye into the leather effects the rate of exhaustion of the dyebath [52], the larger aggregates would be expected to exhaust more slowly than the smaller Orange II monomers. The extremely small amount of dye washed out of the leather by sodium sulfate (Table IV) also indicates that the dye binds only slightly through salt link formation. Therefore steric factors may also be important.

The fourth dye, Red II, is also exhausted more slowly than Orange II from the dye bath. This is undoubtedly due to the large number of solvating sulfonic acid groups of the molecule. Then the ability of the dye to interact with the solvent lessens the rate of reaction with the leather. This effect of decreasing the dyeing rate by increased sulfonation has been demonstrated on wool by Ruggli [39], and Otto [38] has recently pointed out its importance in leather dyeing. However, Otto ascribes the effect of the sulfonic acid groups to screening the available sites for coordinative or secondary bonding by the mobile electrons of the sulfonic acid groups, and the subsequent reduction of this secondary bonding between the dye and the leather. In the case of Red II, it is also apparent from Table IV that large numbers of anionic sites on the dye molecule favor electrostatic bonding, and the mean value for the amount of dye removed by sodium sulfate for Red II is about the same as the corresponding one for Orange II, even though the amount of dye present is much less.

The two pH levels used in the dye bath exhaustion rate study showed a significant difference as may be noted in the data, and this effect of pH on the rate may be attributed to the charge on the leather. At the higher pH, the leather is slightly above the isoelectric point and, carrying a negative charge, may be expected to bind fewer anions than it would with a net positive charge, as at the lower pH [35, 36]. It was also determined that there was no shift of the spectral curve in the region of the absorption maxima for

Orange II and Orange I at the concentrations used in dyeing between the two pH levels. Consequently, the differences cannot be attributed to changes in aggregation of the dyes at these two levels.

The solvents used for effecting removal of the dyes show the expected variations in their means as may be observed in Table IV. The oxalate was extremely active in this capacity, giving evidence that the dye anions did penetrate the complex. However, since sodium oxalate is ionic, part of the dye removed by this agent was probably due to the rupture of electrostatic bonds as well as part being removed by displacement of the dyes from the chrome complex. In this connection, it will be noted that in every case, the oxalate removed more dye from the leather than did sodium sulfate, even considering the latter's greater ionic strength. If the increased amount of dye removed from Red II by sulfate is considered to indicate that most of the dye removed in this same case by oxalate was due to the latter's ionic function, some validation is given to Otto's theory that the amount of dye penetrating the chrome complex is determined by the molecular weight/sulfonic acid group ratio of the dye[37].

Urea was also significantly active in removing dyes from the leather, as evidenced by its high mean value in Table IV. The dye removed in thi smanner was assumed to give an indication of the importance of hydrogen bonding of the dyes to the leather[16, 19, 32]. Fast Red A showed an appreciably larger amount of dye removed by urea than did the other dyes. This was attributed to the increased conjugation (as evidenced by the spectral shift mentioned above)[51] increasing the hydrogen bonding potential of the dye. The mean for urea on Red II, on the other hand, was somewhat lower than that on Orange II. This was probably due to the greater possibility of salt link formation by Red II. Inspection of the data in Table IV also seems to indicate that there may be some hydrogen bonding on the tartrate group of that tannage, since urea apparently removes a slightly greater amount of each dye from this tannage than from the others. However, the absence of a significant wash-tannage interaction term in Table VI restricts the statistical analysis and this could not be substantiated.

If salt link formation were important in the bonding of acid dyes to leather, the amount of Red II removed by sodium sulfate should be greater than that of the other dyes. However, Table IV indicates that this is not the case and that somewhat less Red II is removed than Orange II by the sulfate. Therefore, salt link formation must only be a minor factor in the total picture. It is also noted that an extremely small amount of Fast Red A is removed by sulfate. In this case there is evidence that the formation of hydrogen bonds and penetration of the dye into the complex must be the important forces involved. Also, in view of the difficulty in removing Fast Red A by all the solutions except urea, it is possible that the residual valency forces contributed by the added ring may also be more important with this dye than with the other.

Conclusions

The data presented above indicate that dyeing chrome tanned leather with anionic dyes of the simple monoazo type may be regarded in two steps: (1) The take-up of the dye, or the exhaustion of the dyebath, and (2) the fixation of the dye on the leather.

The exhaustion of the dye bath is influenced by the interactions of the dye and the solvent as well as by the relations between the dye and the substrate. Then, there exists a competition between the leather and the solvent for the dye. The factors which tend to make the dye interact more strongly with the solvent, such as increasing the number of solubilizing groups, and those which decrease the affinity of the dye for the leather (reducing the number of sites available for the reaction by reducing the negative charge on the leather, or increasing the difficulty of complex penetration) act together in reducing the rate of exhaustion of the bath. These same factors determine the amount of dye that will react with the leather in any given time.

Dyes are undoubtedly bound to the leather by a number of different type of bonding forces. The evidence indicates that the penetration of the dyes into the chrome complex and hydrogen bonding between the dyes and the leather are extremely important in this role. Apparently electrostatic bonding, through the formation of salt links, also plays a part, although it does not seem necessary for this type of bond to be formed in all cases. It is strongly suspected, in view of the results of other investigators and from some of the indications in this work, that residual valency, or van der Waal, forces are also important in the total picture. However, complete evidence for this is not available at the present time.

Acknowledgments

The authors with to express their appreciation to the Hilton-Davis Chemical Company, General Dyestuff Corporation, and the Sandoz Chemical Works for the dyes that were used in this investigation. Acknowledgment is also made for the constructive help and criticism of the Director and Staff of the Tanners' Council Research Laboratory and to Miss Helen Steinle for assistance with some of the analysis and statistical calculations.

Statistical Appendix

Tables V, VI, VII, and VIII summarize the statistical analyses that were made on the data presented in Tables III and IV in the main body of this paper.

TABLE V

Analysis of Variance
Dye Bath Exhaustion Rate

Source of Variance	Degrees of Freedom	Mean Squares	F	Significance Level
Dyes	3	1.944	403	0.001
Tannages	3	0.1879	39.0	0.001
pH	1	0.3859	80.1	0.001
Dye-Tannage	9	0.0205	4.25	0.001
Dye-pH	3	0.0362	7.51	0.001
Tannage–pH	3	0.00386	0.80	——
Dye–Tan–pH	9	0.00596	1.24	——
Duplicates	32	0.00482		

TABLE VI

Analysis of Variance
Dye Removal

Source of Variance	Degrees of Freedom	Mean Squares	F	Significance Level
Dyes	3	3.6378	183.7	0.001
Tannages	3	0.1450	7.32	0.001
Wash	3	9.5262	481.1	0.001
Dye-Tannage	9	0.0418	2.11	0.05
Dye-Wash	9	1.4248	72.0	0.001
Tannage-Wash	9	0.0172	0.87	——
Dye–Tan–Wash	27	0.0185	0.93	——
Duplicates	64	0.0198		

TABLE VII

"t" Test on Primary Sources of Variance
Dye Bath Exhaustion Rate

Means Compared	Significance Level
Tannages;	
Unmasked and Formate Masked	——
Unmasked and Tartrate Masked	0.01
Unmasked and Formaldehyde Treated	0.01
Dyes:	
Orange II and Orange I	0.01
Orange II and Fast Red A	0.01
Orange II and Red II	0.01

TABLE VIII

"t" Test on Primary Sources of Variance
Dye Removal

Means Compared	Significance Level
Tannages:	
Unmasked-Formate Masked	——
Unmasked-Tartrate Masked	——
Unmasked-Formaldehyde Treated	0.01
Formate Masked-Tartrate Masked	0.05
Formate Masked-Formaldehyde Treated	0.05
Tartrate Masked-Formaldehyde Treated	0.01
Dyes:	
Orange II–Orange I	——
Orange II–Fast Red A	0.01
Orange II–Red II	0.01
Orange I–Fast Red A	0.01
Orange I–Red II	0.01
Fast Red A–Red II	——
Washing Solutions:	
Water-Sodium Oxalate	0.01
Water-Sodium Sulfate	0.01
Water-Urea	0.01
Sodium Oxalate-Sodium Sulfate	0.01
Sodium Oxalate-Urea	0.05
Sodium Sulfate-Urea	0.01

Questions arose as to the relationship between the amount of dye bound by the leather and the amount of dye removed. An analysis of covariance [10] was run on the data to clarify this point, assuming a linear relationship between the variables. These results are tabulated in Table IX. It will be noted that there was no significant improvement in the precision of the results by this method, and that the same general pattern of "F" is obtained. Therefore, the interpretation of the data using this analysis of covariance leads to essentially the same conclusions as the analysis on the raw data in Table IV.

TABLE IX

Analysis of Covariance
Dye Removal

Source of Variance	Degrees of Freedom	Mean Squares	F	Significance Level
Dyes	3	0.9614	48.95	0.001
Tanages	3	0.05670	2.89	0.05
Wash	3	9.526	485	0.001
Dye–Tannage	9	0.3033	15.44	0.001
Dye-Wash	9	1.4248	72.55	0.001
Tannage–Wash	9	0.01723	0.88	——
Dye–Tan–Wash	27	0.01849	0.94	——
Duplicates	63	0.01964		

TABLE X

Regression Analysis
Amount of Dye Bound vs. Amount of Dye Removed

Source of Variance	Degrees of Freedom	Mean Squares	F	Significance Level
1. Water				
Regression	1	0.3347	43.11	0.001
Residual	30	0.00776		
2. Oxalate				
Regression	1	5.4213	33.94	0.001
Residual	30	0.1597		
3. Sulfate				
Regression	1	2.1542	11.16	0.01
Residual	30	0.1930		
4. Urea				
Regression	1	4.4257	46.24	0.001
Residual	30	0.0957		

TABLE XI

Regression Coefficient Analysis
for Table X

1. Slope of the Regression Line

Washing Solution	Slope
Water	0.22029
Oxalate	0.88662
Sulfate	0.31237
Urea	0.80108

2. "t" Test on Regression Coefficients

Means Compared*	"t"	Significance Level
Sulfate–Oxalate	3.59	0.01
Sulfate–Urea	3.38	0.01
Oxalate–Urea	0.63	——

*Application of the "F" Test showed that the variance of the regression coefficient for water came from a different population than those for the other solutions. Therefore, the "t" Test could not be used.

In order to further clarify the interpretation, an analysis of regression was made on each of the four washing liquors, using the amount of dye bound as the abcissa and the amount of dye removed as the ordinate. It will be noted from Table X that each of these regressions was significant, and application of the "t" test to the regression coefficients (Table XI) as recommended by Brownlee [6], points out some interesting facts. Sodium oxalate and urea which

both act on specific directional bonds group together, while sodium sulfate, which is active with regard to nondirectional charges differs significantly. Water, which is not specific, falls into a class by itself. Thus, some support is apparently given to the use of these solutions for acting on specific bond types.

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Note on the Action of Molds on Fats in Chrome-Vegetable Retan Leather

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In January 1952 we received, from the Quartermaster Corps, U. S. Army, six unworn but badly deteriorated army combat boots, that had been stored in the tropics. The markings on these boots showed that they were produced in 1944 and 1945, by three leading shoe manufacturers. All showed evidence of extensive mold growth. Analyses and tests of cuttings from the vamps and quarters of these boots gave the following results:

	Average	Range	U. S. Army Minimum Specification
% fat, (chloroform extract, dry basis)	6.0	8.6—3.85	18 (1944) 22 (1945)
pH Value (water extract)	2.6	2.65—2.55	3.0
Stitch tear (lbs. per inch thickness)	475	650—275	800
Bursting strength (lbs.)	375	550—215	400

Evidently the leather in each of these boots, after storage for 6 or 7 years, is very far from meeting the specifications for chrome-vegetable retanned upper leather that were in force in 1944-45. While the actual original values for fat content and pH value are, or course, not known, it may be assumed they they met the government specifications. Similar results have been reported by Koppenhoefer [1]. It is at least a plausible assumption that the apparent disappearance of two-thirds or three-quarters of the grease presumed to have been present initially, is attributable to the mold growth. Whether the low values for bursting strength and stitch tear are to be attributed to the loss of fat, or to the low pH values, and whether the low pH values were caused by mold growth, are questions beyond the scope of this note, which deals solely with the action of molds on fat in leather.

Kanagy and his co-workers [2] showed that exposure of vegetable-tanned strap leather to mold growth during soil burial, or in a tropical room, resulted in the disappearance of about 50 per cent of the fat present in the leather before the test. However, exposure to mold growth in a humidity cabinet (85-90° F., 95 per cent relative humidity) caused the loss of not over 20 per cent of the original fat. No other work on destruction by molds of fats in leather has come to our attention, though several authors [3] refer to such action as a well-established fact. In this note we report results of one-year exposure tests of chrome-vegetable retanned Army leather, not treated with *p*-nitrophenol or other fungistatic agent, inoculated with more or less pure cultures of different molds obtained from moldy Army shoes. The results show that the amount of fat destroyed during the test is highly dependent upon the *type* of mold growth.

Procedure

Commercial chrome-vegetable retanned side leather, that had not been treated with *p*-nitrophenol, was furnished by Pfister & Vogel Tanning Co. A portion was ground and analyzed for water, fat (chloroform extract) and pH value, and the extracted fats were further analyzed for free fatty acids.

Molds from the returned Army shoes were cultured on Sabouraud's Dextrose Agar. White, green, and black colonies were isolated.

Strips of the leather were inoculated with spores from these 3 types of colonies, and were incubated for one year, in separate containers, in the dark, at approximately 100 per cent relative humidity, at room temperature (about 70 to 90° F.). A fourth strip was incubated without inoculation, but this strip, like the inoculated strips, developed profuse mold growth, evidently from air-borne contamination. The growths on the three inoculated strips were mostly, but not entirely, of the color of the inoculant. The growth on the non-inoculated strip was white. After one year, the mold growth was brushed off, and the strips were air-dried, ground, and analyzed for water, fat, free fatty acids, and pH value. The original analytical sample, which had been stored in a closed container,was re-analyzed.

Results

The following table shows the analytical results obtained:

Changes in Fat Content after One Year Exposure to Mold Growth

Sample No.	Treatment	Total Fat: % in dry leather	Total Fat: % change during exposure	Free Fatty Acids: % in dry leather	Free Fatty Acids: % change during exposure	Free Fatty Acids: % in total fat	pH Value
1*a*	As received	26.5	——	1.23	——	4.6	3.3
1*b*	After storage (sealed) for one year	25.8	−2.6	0.96	−22.0	3.7	3.35
2	Not inoculated; stored at 100% relative humidity for one year; heavy mold growth, prevailingly white	12.3	−52.5	0.41	−66.6	3.4	2.8
3	Same treatment; inoculated with black mold	22.8	−13.9	2.02	+64.2	3.0	3.0
4	Same treatment, inoculated with white mold	16.3	−38.4	0.47	−61.7	2.7	2.7
5	Same treatment, inoculated with green mold	22.4	−15.4	1.35	+9.8	6.0	2.9

The leather sample stored in the dry state lost a negligible amount of fat. The apparent loss in free fatty acids, which amounts to only 0.27 per cent, on the leather weight, but represents 22 per cent of the initial free fatty acids, may be due to fixation of fatty acids during storage, or may simply reflect lack of precision of the method.

The changes in amount of fat, and in fatty acids, in the leathers exposed to mold growth, are strikingly dependent on the prevailing type of mold. In the case of the black and the green molds (sample 3 and 5) there is a moderate decrease in total fat (about 15 per cent), which in itself would hardly affect the strength of the leather. There is an increase in free fatty acids, especially in Sample 3, though here again the levels reached do not appear to be excessive. But in the case of the white molds (Sample 2 and 4) the destruction of fat amounts to one-half and three-eighths respectively, of the amount present initially, and there is an even greater proportionate destruction of free fatty acids.

The pH values of the aqueous extracts of all the leathers (except the stored analytical sample) declined during exposure, and the decline appears to be greatest for the white molds.

Mr. W. M. Higby, Chief Chemist of Horlick Corporation, Racine, identified the molds as to type as follows:

Sample 3 (prevailingly black): *Aspergillus niger*
Aspergillus glaucus

Sample 5 (prevailingly green): *Penicillium glaucum* (chrysogenum?)
Penicillium olivaceum

Samples 2 *and* 4 (prevailingly white): *Aspergillius glaucus* (not abundand) A symbiotic growth of *P. glaucum* (nonsporulating) and and unidentified bacterium producing a yellow pigment.

The white mold proved to be quite a problem to identify, because, while mycelia were very numerous, no spore formation was in evidence. By repeated platings it was finally established that it is a symbiotic growth of bacteria and one or more molds. (Symbiotic means that the two entities are mutually dependent). The presence of the bacteria seems to prevent spore formation of the molds, but does not inhibit copious growth of mycelia. When the bacteria were removed, the mold reverted to *Penicillium glaucum* (the blue-green mold). The bacterium was not identified, but produced a strong yellow color.

Since it was in the presence of this symbiotic growth that marked destruction of fats, and free fatty acids, occurred, it may be suggested, as a working hypothesis, that the mold splits the fats, and that the bacterium then destroys the liberated fatty acids. Further investigation, by professional mycologists, of this interesting biological problem, would be of value. We are now repeating the test, using leather containing *p*-nitrophenol, to see whether this fungistatic agent is equally effective against all the types of molds that we have isolated.

The authors wish to express their thanks to Mr. Adolf Schubert, who suggested this study, and to Mr. H. E. Ellison and others of the staff of B. D. Eisendrath Memorial Laboratory for analytical assistance.

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ABSTRACTS

The Recovery of Wool Wax from Wool Scour Liquors. By L. F. Evans and W. E. Ewers. *Australian J. Applied Sci.* **4**, 552 (1953). A process has been developed for the recovery of wool wax from wool scour liquors. The liquors are aerated in flotation cells, the froth formed being recirculated through the impellers of the cells in order to make the

wax in the froth more granular and the froth less bulky. The froth is then washed by passing it in counterflow with wash water through two more flotation cells. The washed concentrate contains about 10 per cent wax, which on draining rapidly increases to 20 per cent. This concentrate is dispersed in an alkaline medium to give a concentrated emulsion from which good quality wool wax is obtained by centrifuging. The overall recovery of wax depends on the wax content of the liquor. For a scour liquor containing 1.5 per cent wax a recovery of 48 per cent would be typical, 40 per cent being lost in the aeration stage and another 12 per cent during the separation of wax from the froth dispersion. While the method has been developed using liquors from soap-soda scours, preliminary tests indicate that it could be applied equally well to liquors containing the synthetic detergents, "Lissapol N" and "Teepol". The process is already being applied successfully on a commercial scale.

Fellmongering Investigations. XVII. Improved Water Digestion of Sheepskin Pieces by Aeration and the Addition of Calcium. By W. G. Crewther and T. A. Pressley. *Australian J. Applied Sci.* **4**, 344 (1953). The effect of the addition of nutrient media, bacterial culture, and metallic ions on the rate of digestion of sheepskins in warm water under aerobic and anaerobic conditions has been followed on a laboratory scale. Aeration of the digest gives the most rapid digestion, especially if the liquor contains at least 0.01 *N* calcium. The addition of nutrients such as peptone increases the rate of digestion, whereas in the presence of glucose the pH falls and the digestion becomes very slow. Of the bacteria tested, selected strains of *Aerobacillus polymyxa* cultured on wheat mash gave most rapid digestion and exceptionally white wool. The methods above outlined are unsuitable for the digestion of pieces from skins which have been treated with depilatory paint, but these are digested rapidly after neutralization and pretreatment with a protease solution.

Aspergin. By B. Vitar. *Koza I Obuca* **2**, 4 (1953). The Institute for Industrial Research of Zagreb has produced a suitable dye for leather from *Aspergillus oryzae* grown on rice. It is marketed under the trade name of Aspergin.

Leather Tests. By B. Glozic. *Koza I Obuca* **2**, 9 (1953). This is the first of a series of papers on the analysis of tannery solutions, auxiliary agents and leather. In the present paper the author deals with the analysis of beam house chemicals.

Tanning of Upper and Sole Leather with Mixed Vegetable and Chrome Tanning Materials. By I. Restek. *Koza I Obuca* **2**, 93 (1953). Characteristics of this kind of tanning, its methods, and its theory are given in the article.

Tanning Sole Leather with a Blend of Seventy-Five Per Cent Vegetable Tans and Twenty-Five Per Cent Synthetic Tans. By F. F. Marshall and H. G. Turley. *Leather Manuf.* **64**, No. 10, 9 (1953). A quantity of steer bends and shoulders was tanned on a pilot plant scale, with a blend of 75 per cent vegetable tannins and 25 per cent orotan. Hide passed through 16 rocker liquors and two layer liquors. Tannin content of the tail rocker was 0.86, the head rocker 7.93, the first layer 6.70 and the second layer 7.87 per cents tannin respectively. The total tanning time of tanning was 51 days. The yield was

248.4 pounds of leather per hundred pounds of tannin. The degree of tannage and load were less than normal. During the tanning operation it was noted that the tan liquors contained less insolubles than are normally present in a straight vegetable liquor. The pH of the liquors did not show the necessity for addition of acid, and evidently the presence of the syntan in the tan yard imparted sterile qualities to the leather as it withstood mildewing tests for at least five months.

Estimation of Cholesterol and Triterpenols in Unsaponifiable Fraction of Wool Wax. By H. Duewell. *Anal. Chem.* **25,** 1548 (1953). The author describes a modification of Lederer and Tehen's procedure which permits the simultaneous determination of cholesterol and triterphenols. The modified method is both accurate and rapid.

Rapid Precipitation of Barium Sulfate. By R. B. Fischer and T. B. Rhinehammer. *Anal. Chem.* **25,** 1544 (1953). The light microscope and electron microscope techniques were used in the study of barium sulfate precipitation. The study led to the development of two procedures, either of which offers no improvement over the conventional method except in the saving of time. The procedure recommended is as follows: $BaCl_2$ solution, 0.02 *M*, is prepared from reagent grade salt and the solution is allowed to stand at room temperature at least 24 hours prior to use. Sulfate solution is 0.006 to 0.16 *M*, preferably about 0.01 *M*. The pH of the sulfate solution is adjusted to 1 with HCl, unless alkali salts are present in high concentration, in which case pH is adjusted to 5. Total volume of reagents is 150 to 200 ml. Temperature is 95°C. for solutions. $BaCl_2$ solution is poured rapidly into sulfate solution. An initial 10-20 per cent excess of $BaCl_2$ solution is used, although more may be added just prior to filtration if desired. Vigorous hand stirring is employed for 2 or 3 minutes. No digestion period is necessary, other than a few minutes to allow the beaker to cool. Filtration is rapid, only very brief washing is necessary, and ignition over burner for 20 minutes at 600° to 800°C. Finally, the precipitate is weighed.

Quercetin as Colorimetric Reagent for Determination of Zirconium. By F. S. Grimaldi and C. E. White. *Anal. Chem.* **25,** 1886 (1953). Quercetin has been found to yield a sensitive color reaction with zirconium, suitable for the determination of 0.1 to 50 γ of zirconium dioxide. It thus forms the basis for a colorimetric method devised by the authors for the determination of small amounts of zirconium.

The Coloration of Leather. By J. R. Blockey and D. H. Tuck. *J. Soc. Dyers and Colourists* **69,** 273 (1953). The authors discuss the structure of hide and the effect of its modification through the preparatory and tanning processes as related to its dyeing. Dyeing requirements, such as fastness to wet and dry rubbing and fastness to perspiration and light, fullness of color, penetration, and levelness of color, are dealt with. The use of acid and basic dyes as related to specific leathers, dyeing methods, and the use of auixiliary agents in the dyeing process complete this portion of the article. Pigment finishing completes the survey of leather coloration.

Materials of Construction for Chemical Engineering. *Ind. Eng. Chem.* **45,** 2171 (1953). This seventh edition of the Society's Annual Materials of Construction Review surveys the recent developments, as reported in the published literature in the use of thir-

teen construction materials. Thirteen articles comprise the Review. The abstract which follows is supplementary.

Properties of Chemical Engineering Materials of Construction. *Ind. Eng. Chem.* **45,** 2270 (1953). This is the fifth in the series of annual tabulations of the properties of chemical engineering materials of construction which have been published with I. and E. C.'s Materials of Construction of Review since the second edition of the feature. Information this year is mainly supplementary to the contents of preceeding tables. The materials considered are aluminum alloys, carbon and graphite, cements, iron, mild steels, low alloy steels, nickel and high nickel alloys. Reprints of the full report can be obtained from the Reprint Department of the ACS. at a nominal price.

Solvent Tannage. By F. O'Flaherty. *Lea. and Shoes* **126,** No. 18, 22 (1953). Although solvent tannage was considered as long ago as 1911, it did not receive the serious attention now being directed toward it. Reasons for the present interest are high labor costs and their inflexible character, more control of process and product to meet the exacting and rapidly fluctuating demands of the trade, and the output of a more uniform product. The cost of solvent tannage equipment would no doubt be considered high in comparison with equipment cost of a normal plant, but when measured against high labor costs and rapidity of output, amortization of solvent tannage equipment in a reasonable time may be possible. There are numerous problems besides amortization which have yet to be solved from a practical production standpoint.

Leather Color and Water Repellence. By C. C. DeWitt. *Leather and Shoes* **126,** No. 18, 25 (1953). It is suggested that a product be made which is both a dye and a water repellent, which will neither crock nor destroy the porosity of the leather.

Syntans. By W. S. Short. *Tanner,* **7,** No. 12, 17 (1953). The author briefly discusses the structure, properties, and tanning action of syntans. He divides syntans into two classes: (1) Those in which the phenolic hydroxyl groups, if present, exert little or no effect upon collagen and whose tanning action is dependent on sulfonic acid groups; (2) Those in which the phenolic hydroxyl groups are the effective tanning groups and in which the number of sulfonic acid groups must be kept to a minimum. In practice the first group is used as auxiliary tannins to speed up penetration, disperse phlobaphenes, and improve color. The second group acts as replacement tannins. While natural tannins probably contain more hydroxyl groups than the replacement tannins, it is also probably true that all are not equally effective. The tanning action of a syntan can be improved by increasing the number of its hydroxyl groups, but the procedure involves the use of too expensive polyhydric phenols.

Plastic Finishes. By J. Ghosh. *Tanner* **7,** No. 8, 11 (1953). The future of the Indian upper leather industry depends on making full use of fallen hides, even though these have poor substance, are veiny, and are damaged by bacterial action. Different types of corrected grain finish are, therefore, essential. Since glazing accentuates grain defects, this step must be omitted. While mucilage-casein base and shellac-albumen sopping could be standardized with respect to the finishing, acrylic resin dispersions have proved to be the

easiest to prepare, and the most satisfactory due to finer film deposit and filling up of uneven buffed surfaces. To standardize the stretchiness, flexibility, and other useful factors of a finish, it is customary to polymerize together different monomers, the hard type, methyl acrylate and the soft type, ethyl acrylate, in the proportion of 80-20. When the proportions are reversed, a highly flexible soft film with less gloss and higher extensibility is obtained. For leather finishes it is common practice to mix pigment with an aqueous dispersion of suitable monmers. Catalysts such as peroxides or polysulfides are chosen according to suitability and the polymerization is carried out in the presence of surface active agents. Plasticizers are also employed. Particle size of the polymerized molecule is influenced considerably by the nature of the pigment paste and plasticizers incorporated during the preparation of the resin. A high percentage of inorganic salts affects the polymer size and may break the dispersion of the resin. Resin emulsions precipitate in acid pH and give a good film. It is common practice to spray skivers with acetic or formic acid prior to the application of the resin emulsion, thus assuring a satisfactory film. Particle size is very important, and should vary according to the type of leather being finished.

Oils and Fats in the Leather Industry. By M. B. Das. *Tanner* **7**, No. 10, 11, No. 11, 16 (1953). The natural vegetable, animal, and fish oils in use in the tannery are first listed. These are followed by the fats of animal origin, waxes of petroleum, and finally the German synthetic oils developed in Germany during the war. The function of the oils is then briefly described. The shortage of fish oils in India has led to a research program to develop a satisfactory substitute.

Standards for Leather Manufactured in India. By M. Banerjee and P. K. Sarkar. *Tanner* **7**, No. 8, 15, No. 10, 27, No. 11, 11, No. 12; 10 (1953). Since India produces about one-fifth of the world's output of hides and skins, and tans 90 per cent of her buffalo hides, 78 per cent of her cattle hides, 94 per cent of her sheepskins, and 20 per cent of her goat skins, it is highly important that standards be set up for the various leathers produced. Standards should be both chemical and physical. In order to establish a basis for standards, analytical and physical data had to be collected, and preliminary to this, the authors set forth methods to be employed. Certain data have accordingly been collected, and tentative specifications set up in conformity with the data. The leathers coming under these specifications are chrome tanned box and willow kips and sides for shoe uppers, glazed kid, chrome lace leather, russet leather, sole, belting and harness leathers, and chamois leather.

An Investigaion on Bleaching of Vegetable Tanned Light Leathers. By J. K. De. *Tanner* **7**, No. 7, 15 (1952); **8**, No. 8, 27 (1953). Crust sheepskin leathers were drum bleached as follows: (1) 5 per cent hypo in 100 water for 30 minutes at 40°C., followed by 4.4 per cent commercial HCl for 15 minutes; (2) 2 per cent $NaHSO_3$, 100 per cent water for 30 minutes at 40°C., followed by 2.2 per cent HCl; (3) fresh myrobalam liquor of 5°Bk., adjusted to pH 3.0 for one hour, then kept in liquor overnight; (4) same, except Bk. was 10°; (5) 7 per cent Tannigan F.C.B.I. for 35 minutes at 40°C; (6) 3.8 per cent borax, 100 per cent water for 30 minutes at 40°C., solution replaced with 2.5 per cent oxalic acid and 50 per cent water for 15 minutes; (7) 1.25 per cent oxalic acid and 25 per cent water brushed on grain until solution was consumed. All per cents are on leather weight, and all leathers were washed after bleaching. It was concluded that drum bleaching is not

satisfactory; that the bleaching effect is largely due to removal of superficial tannins by the alkalies, and color subsequently brightened by the acid treatment; that oxalic acid makes a whiter leather than HCl; that syntans like Tannigan F.C.B.I. can bleach more uniformly than the other agents, and a combination of the syntan and oxlic acid should give the best results; that myrobalam liquor imparts a yellowish tone without bleaching; that treatment with oxalic acid and myrobalam liquor weakens the leather.

A second test was made by vat dipping crust vegetable tanned light buffalo calves. Percentage of chemicals is on the dry leather weight. Tests were as follows: (1) 5 per cent hypo, 50 per cent water at 40°C. for 30 seconds, followed by second bath of 14 per cent HCl (22°Tw.), 50 per cent water, for the same time duration; (2) 2 per cent $NaHSO_3$, followed by 2.2 per cent HCl and 25 per cent water; (3) 5°Bk. myrobalam liquor at pH 3, adjusted with HCl and alum for 1 hour, and then over night; (4) 7 per cent Basyntan F.C.B.I. and 100 per cent water for 30 seconds; (5) 3.8 per cent borax, followed by 2.5 per cent oxalic acid and 50 per cent water; (6) 2.5 per cent oxalic acid and 50 per cent water; (7) 5 per cent Basyntan and 2 per cent oxalic acid for 30 seconds at 40°C.; (8) 3.8 per cent borax and 100 per cent water, followed by second bath of 2.5 Basyntan F.C.B.I., 100 per cent water, and 1.25 per cent oxalic acid. It was concluded that vat bleaching is superior to drum bleaching; that the best method is to use two baths, the first to consist of borax, and the second of syntan like Basyntan F.C.B.I. and oxalic acid. Reagents which liberate SO_2 have no special virtues as bleaching agents.

Sulfite Cellulose Extract in the Tanneries. By O. Skaar. *Tanner*, **7**, No. 10, 22 (1953). Experiments are described where Totannin (ammonium lignosulfonate) replaced up to 25 per cent of the 100 wattle and chestnut extracts, respectively. Increased degree of tannage and weight gains occurred when the sulfonate replaced wattle but the opposite was true where the sulfonate replaced chestnut.

The Application of Impulse Rendering to the Animal Fat Industry. By I. H. Chayen and D. R. Ashworth. *J. Appl. Chem.* **3**, 529 (1953). The impulse rendering process, which consists in mechanically rupturing membranes of fat containing cells by high speed impulses transmitted through the medium of a liquid, has been developed mainly for degreasing animal by-products in such a way as to preserve the quality of the fat and protein. The degreasing of bone and soft fat is described in some detail, and brief reference is made to possible applications in the recovery of oils from fish and fish livers.

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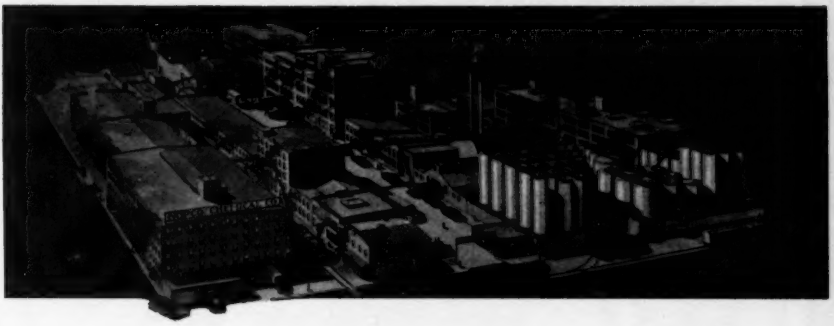

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